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SOIL SCIENCE

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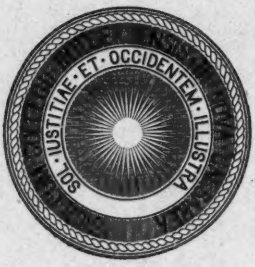

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A NOTE ON THE PROTOZOAN FAUNA OF THE SOILS OF THE UNITED STATES

R. V. ALLISON

Rothamsted Experimental Station

Received for publication March 10, 1924

The theory developed by Russell and Hutchinson in 1909 that a "biological factor" is concerned in the characteristic reaction of the microflora of the soil after partial sterilization, has served as the basic stimulus for a tremendous amount of research upon this subject in several different countries. In this, as is well known, the consistent indictment of the protozoan fauna as a factor of prime importance has been most emphatic.

An excellent review of the theories developed previous to, and contemporaneously with that of Russell and Hutchinson has been presented by Kopeloff and Coleman (7) and covers the literature to 1917. In this, they also treat, in a general way, the application of protozoology to the study of the highly complex relations of the microfauna of the soil to the numerous other forms of its microscopic life.

In this question, as in any other of similar nature investigated under widely different conditions, particularly of materials and technique, one finds in the literature certain points of difference that have arisen among the various investigators. Most important among these is that which relates to the actual significance of the presence of a trophic protozoan fauna to the prosperity and efficiency of the bacterial flora. The nature and extent of these controversies and the methods used have been fully reviewed to the date indicated above. It might be noted that American investigators, by no means, have been delinquent in the presentation of data which has seemed strongly controversial to the general theory.

The writer has brought together more than a score of soil samples from widely different points in the United States for the purpose of examining the protozoan fauna according to the methods now in use in the protozoological department, Rothamsted Experiment Station. Each sample was taken by a member of the staff of a state experiment station, placed in a half-pint jar and sealed with a cork-lined, screw-top lid in such a way that the moisture content of the soil as found under field conditions was maintained. In two cases the samples submitted were air-dried. It is a pleasure to thank the workers in the various states for their kind cooperation in the collection of the material. The necessity of taking into consideration the age of the samples and the conditions under which they were held prior to examination is fully emphasized in the in-

terpretation of the results. Particularly for this reason they were studied largely from the qualitative standpoint though a limited number of quantitative examinations were made.

Cutler (2) at Rothamsted has insisted upon the necessity of first gaining some knowledge of the activities and life histories of the soil protozoa before attempting to discover what part they may play in partial sterilization. He has therefore spent sometime in developing standard methods of technique for the counting of protozoa. As a result a method was derived by which it was possible to count the total numbers of the organisms in a soil sample, and further to distinguish between the numbers of active and cystic forms.

Such a differentiation is of prime importance, for it may easily happen that a soil sample may contain large numbers of protozoa the majority of which are in the cystic condition, and unless this is known any conclusions which are drawn relevant to total numbers are almost certain to be erroneous.

This method was given its first extensive application when Cutler, Crump, and Sandon (6) made a daily count of protozoan and bacterial numbers from a described area of "Barnfield." (the classical Root field) through a period of 365 days. This was done in order to discover the relationships between the various members of the soil population under field conditions. The information thus collected upon protozoan as well as bacterial numbers doubtless constitutes the largest body of homogeneous data upon this subject that has been prepared to the present time. With such a mass of data available, it was found practicable to apply statistical methods in its organization and interpretation. By this means certain deductions have been made possible concerning the relations between the periodicity of the bacterial and of protozoan numbers as well as the relation of these fluctuations to changes of season and climate.

An important fact at once evidenced by the investigation was that the numbers of bacteria showed large daily variations, and did not remain constant for long periods of time as had been assumed. Prior to this investigation workers had not hesitated to consider comparable the counts of bacterial numbers in soil samples taken at different periods, sometimes separated by long intervals of time.

Such a procedure is open to grave objections in view of the daily variations that are now known to occur.

The nature and extent of these changes for a single protozoan type compared with bacterial numbers is indicated in figure 1. Here the opposing influence of protozoa to bacteria is well illustrated where Dimastigamoeba and species α either alone or together stand opposite to practically every change in bacterial numbers. According to a contingency table prepared upon the relation of these diverse groups of organisms, the fluctuations in bacterial numbers were found to be explained by the counter tendency of the numbers of these two species of amoeba, acting either alone or together, in eighty-six per cent of the cases. These results would appear to dispose of the earlier

claim as to the existence of the protozoan fauna of the soil in an inactive state and further indicate that, when present, it is of unquestionable significance in its influence upon bacterial numbers.

This view is strengthened by the inoculation experiment of Cutler (3) who was able to reproduce the daily fluctuations in numbers by inoculating sterile

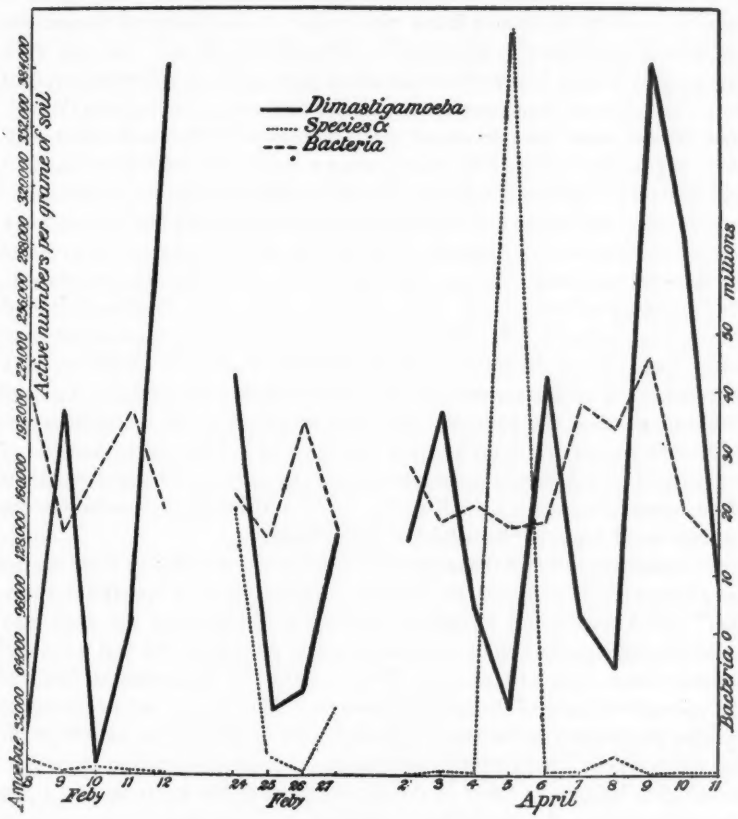

FIG. 1. NUMBERS OF ACTIVE AMOEBAE (DIMASTIGAMOEBA AND SP. α) AND BACTERIA IN 1 GM. OF FIELD SOIL FOR TYPICAL PERIODS IN FEBRUARY AND APRIL
Cutler, Crump and Sandon (6, p. 333)

soil with bacteria and protozoa. In similar soil cultures inoculated with bacteria alone the variations in numbers were not observed.

The violent fluctuations in protozoan numbers that have been observed independent of season under field conditions could not be accounted for by any of the more rigorous climatic changes occurring within the year. This fact has led to studies of the rates of reproduction of individual types in pure

culture under rigidly controlled conditions in the laboratory. These studies, still in progress, reveal results of great interest and disclose a periodicity quite in keeping with that found under field conditions (4,5).

The conclusions arrived at in the more recent work of Waksman and Starkey (8) may be regarded, on the other hand, as representative of the attitude taken by a considerable number of American workers towards the importance of the activity of the protozoan fauna with respect to the biological phenomena that appear consequent to the partial sterilization of the soil. In this work they studied, in part I, samples of Sassafrass loam soil from differently treated plots which, by continuous fertilizer treatment and systematic cropping through some fifteen years, have developed sharp differences in their individual crop-producing power. In part II, they studied a soil of the same type that had been held under uniform conditions of moisture and temperature in the laboratory for more than eleven months and through this treatment had become more or less homogeneous in its physico-chemical balance and constant in so far as the biological equilibrium among the different groups of micro-organisms and their activities was concerned. In part III, the same type of soil as that used above was examined for the ability of its flora to decompose organic substances before and after partial sterilization by different means. In all of this work the influence of various treatments, particularly of different methods of partial sterilization, upon the biological activities occurring in the material under study was interpreted largely upon the basis of careful determinations of evolution of carbon dioxide in conjunction with the progressive transformations of nitrogenous materials as well as the significant changes in numbers in the various broad types of the solid microörganisms.

In the interpretation of the rather considerable data afforded by these studies the authors have concluded that the characteristic effect of "partial sterilization" which was found to appear consistently throughtout the work may be attributed equally well or even better to the activity of the soil fungi and actinomycetes than to protozoa. They regard the fundamental basis of the unusual response of the bacterial flora that follows such soil treatment as existing particularly (*a*) in the chemical changes in the organic matter of the soil which render it more readily assimilable, (*b*) in the disturbance of the microbiological balance in favor of the development of the bacteria, and (*c*) in the redistribution of potential food substance formerly existing as protoplasm in the bodies of active organisms of various types but which have been destroyed by the treatment. Upon this basis, the secondary tendencies which follow would be explained largely by the direct competition of the different surviving types for the more or less limited quantity of available food material as well as the fundamental differences among these types in their response to such materials as are available and the variability of their respective efficiencies in the use of such. The diversity of these conclusions particularly as regards the importance of the protozoan factor, will be discussed below.

TABLE 1

Description of soils studied

STATE	SOIL†	REMARKS
Virginia	Hagarstown loam	Derived from Dolomitic lime-stone rock
South Dakota	Barnes fine sandy loam	"No treatment," plot 140, complete fertility investigations
Illinois	Tama or brown silt loam	Common corn belt soil taken from corn-field under cultivation
Indiana	Sioux silt loam	From under grass at Experiment Station
Kansas	Oswego silt loam	Generally cropped, shale derivation sub-soil hard and impervious
Iowa	1. Carrington loam	From Agronomy farm at Experiment Station
	2. Webster silty clay loam	From Agronomy farm at Experiment Station
Colorado	(a rather heavy loam)	Section 300, Department of Agronomy, Under rotation of corn, oats, and fallow (1923).
Kentucky	Maury silt loam	High phosphatic Trenton Soil. Last crop was corn preceded by clover.
Utah *	Greenville loam	Plot 73-G.A., Experiment Station farm. Under culture 40–50 years. Last 10 years received 10 T. manure and 40 in. irrigation water annually.
Tennessee	1. Cumberland loam	Cowpea-wheat rotation, unfertilized for 18 years
	2. Cumberland loam	Same soil in cylinders since 1913 with 8 T. hydrated, precipitated $MgCO_3$ per acre
Ohio	1. Yellow sand loam	Shallow sandy top soil, moderate organic content. Under grass.
	2. Yellow sandy loam	Subsoil of (1) Yellow sand, no organic matter.
Texas*	Lufkin fine sandy loam	Surface soil, College Station
Pennsylvania	Hagarstown silt loam	From vegetable garden, heavily fertilized (commercial and farm yard manure)
Massachusetts	Merrimac fine, sandy loam	
Minnesota	Clarion silt loam	Glacial drift, sub-soil yellow silt, moderately heavy and calcareous. From wheat field.
Wisconsin	Miami silt loam	Field plot B. 6 of four-year rotation of clover, corn, oats, wheat. 8 tons manure on corn and 8 tons on wheat
California	Dublin clay adobe	Largely alluvial wash from Altamont clay or clay loam. Faculty Club garden

TABLE 1—*Continued*

STATE	SOIL†	REMARKS
Louisiana.....	Loessial silt loam	Continuous corn since 1889. Commercial fertilizer without organic matter to 1908. Cottonseed meal, acid phosphate and 8 tons of manure every three years. Cowpeas turned under with residue every year
Washington.....	Palouse silt loam	Typical wheat soil of east Washington. Rotation, wheat and fallow, residue returned
New Jersey.....	Sassafrass loam	A very light loam with coarse sandy subsoil. Nitrogen availability series at the Experiment Station. Acid phosphate and muriate of potash. In addition: 5A—cow manure 5B—cow manure plus lime 9A—nitrate of soda

*Air dry.

† Most of the samples were taken about the middle of July.

SOURCES AND TYPES OF SOIL STUDIED

The manner in which the soil samples were taken has been indicated above. Most of them were brought over as luggage and a considerable time thus saved in the necessary period which elapsed before their examination. It was thus possible to start working with them promptly upon arrival at the laboratory about August 1. Even so, some of the samples had been sealed a month or longer before the studies which have been recorded were made. In studies here at Rothamsted, the history of the soil, particularly in regard to its manurial treatment, has been found most useful in understanding the diversity of the fauna in soils of different origin. For this reason such information as to type and previous fertilizer treatment and cropping as was submitted with the various samples is presented in table 1. Subsequent reference to these samples in the text will be according to the state from which they were obtained.

QUALITATIVE STUDIES

In the qualitative studies of the samples the practice was to examine them both in hay infusion and upon agar, the latter being prepared in duplicate cultures. Following the preparation and sterilization of the media and its distribution in sterile petri dishes, 5-6 gm. of the moist soil were transferred to each culture by means of a sterile spatula.

The hay infusion was prepared by boiling 50 gm. of chopped hay with one liter of distilled water, filtering and clearing in the usual way with final

Qualitative studies upon the protozoan fauna of the soil samples described in table 1

SOIL SAMPLE	FLAGELLATA*									FLAGELLATA			RHIZOPODA			
	Cercomonas	*Heteromita lens*	*H. globosus*	*Sainouron*	*Oicomonas*	*Spiromonas*	*T. spiralis*	*T. rostratus*	*Allantion*	*Colpoda cucullus*	*Colpoda steinii*	*Gastrostylus*	*D. gruberi*	*Sp. (alpha)*	*Chlamydophrys*	*Nuclearia*
Virginia	+	+	+	+	+	+	+	−	−	+	+	−	+	+	+	−
S. Dakota	+	+	+	+	+	−	−	−	+	+	+	−	+	+	+	+
Illinois	+	+	+	+	+	+	+	+	+	+	+	−	+	+	+	−
Indiana	+	+	+	−	+	+	−	−	+	+	+	−	+	−	−	−
Kansas	+	+	+	−	+	−	+	−	−	+	−	−	+	+	−	+
Iowa 1	+	+	+	−	+	−	−	−	+	+	−	−	+	−	−	−
Iowa 2	+	+	+	+	+	+	+	−	−	+	+	+	+	+	+	−
Colorado	+	+	+	−	+	+	+	+	+	+	+	−	+	+	+	+
Kentucky	+	+	+	−	+	=	+	−	+	+	+	+	+	+	+	+
Utah	+	+	+	+	+	+	−	−	+	+	+	+	+	+	+	−
Tennessee 1	+	+	+	−	+	−	+	−	−	−	+	−	+	+	−	−
Tennessee 2	+	+	+	−	+	+	−	−	−	−	−	−	+	+	−	−
Ohio 1	+	+	+	+	+	+	+	−	+	+	+	−	+	+	+	+
Ohio 2	+	+	+	−	+	−	−	−	−	−	−	−	−	−	−	−
Texas	+	+	+	+	+	+	+	−	−	+	+	+	+	+	+	−
Pennsylvania	+	+	+	+	+	+	+	−	−	+	+	−	+	+	+	−
Massachusetts	+	+	+	+	+	−	+	−	−	+	+	+	+	+	+	+
Minnesota	+	+	+	+	+	+	+	−	+	+	+	+	+	+	−	+
Wisconsin	+	+	+	+	+	+	+	−	+	+	+	−	−	+	−	−
California	+	+	+	+	+	+	−	−	+	+	+	+	+	+	+	−
Louisiana	+	+	+	−	+	+	+	−	+	+	+	+	+	+	−	+
Washington	+	+	+	−	+	−	−	−	−	+	+	+	+	+	−	−
New Jersey	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	−
Total	20	20	20	13	20	15	15	3	13	19	19	10	19	19	13	8
Per cent	100	100	100	65	100	75	75	15	45	95	95	50	95	95	65	40

* The plus sign indicates the presence of the organism concerned in either or both of the media used.

fractional sterilization in the steamer. Before using, this was diluted 50 per cent with sterile tap water. In the case of the solid substratum, ordinary nutrient agar was used with the addition of 1-2 cc. of sterile tap water after introducing the soil. Investigations upon the response of protozoa to variations of reactions in the substratum seem to indicate that practically all types thrive well throughout a considerable range of hydrogen-ion concentration on either side of neutrality.

The cultures were examined at the end of the first and second week and in some cases at the end of the third week. The results of these studies upon the various samples are given in table 2. Only the more common genera of the general groups Flagellata, Ciliata and Rhizopoda are recorded.

For the sake of comparing the population of these samples qualitatively with that of English soils such as have been studied at Rothamsted, it was thought desirable to give particular attention to those types whose numbers have been found significantly high in the extended experiment discussed above. Thus of the samples from twenty different states that were examined, 100 per cent were found to contain *Heteromita* sp., *Cercomonas* sp., and *Oiconomas* sp., 95 per cent were found to contain *Dimastigamoeba gruberi* and Species α, while *Sainouron*[1] (earlier referred to asγ) was found in 65 per cent of the samples. A number of the other forms, particularly of the ciliata, are likewise found to appear in a large proportion of the samples.

Besides those noted in the table, mention might be made of the flagellate *Parapolytoma* sp. found in the Minnesota and California samples and *Actimonas* sp. found in the Ohio sample (top soil) and of the ciliates *Cyclidium* sp. found in the Washington and Massachusetts and *Halteria* noted in the Minnesota sample. Without doubt if all cultures had been examined after four weeks. as well as after two, numerous other forms would have appeared consequent to the disappearance of these noted.

QUANTITATIVE STUDIES

In the study of the samples from a quantitative standpoint Cutler's method described and used in the earlier work in this laboratory was employed. Sufficient of the data obtained upon total numbers will be presented to indicate the nature of the results and demonstrate the method which will be briefly described. As stated above, consideration must be given, particularly in the interpretation of the results, to the treatment of the sample prior to examination.

THE METHOD

The difficulty of separating protozoan cells from the soil mass in which in some way, they are firmly held by the soil particles, has been recognized since the earliest investigations upon this subject. This peculiar power of the soil to

[1] See Sandon, H., 1924, *In* Jour. Linn. Soc., v. 35, p. 449–475.

retain these and other cells has always proved sufficient to render all attempts to make direct counts of the protozoan (1) fauna ineffective. It was for this reason that the method now in use was developed, on the dilution basis.

In the development of a systematic procedure for the routine preparation of soil samples for counting the protozoan fauna by such a method, the prac-

TABLE 3

Number of soil organisms per gram of soil corresponding to the number of negative plates in the three dilution series indicated

From Cutter, Crump, and Sandon (6, p. 341)

1 DILUTIONS 25:102,400		2 DILUTIONS 50:204,800		3 DILUTIONS 50:409,600	
Number of sterile plates	Protozoa per gram	Number of sterile plates	Protozoa per gram	Number of sterile plates	Protozoa per gram
1	110,000	1	220,000	1	420,000
2	59,000	2	118,000	2	230,000
3	36,000	3	72,000	3	140,000
4	23,000	4	46,000	4	95,000
5	16,000	5	32,000	5	64,000
6	11,000	6	22,000	6	44,000
7	7,600	7	15,200	7	30,000
8	5,300	8	10,600	8	21,000
9	3,700	9	7,400	9	15,000
10	2,600	10	5,200	10	10,000
11	1,800	11	3,600	11	7,300
12	1,300	12	2,600	12	5,100
13	900	13	1,800	13	3,600
14	640	14	1,280	14	2,600
15	450	15	900	15	1,800
16	320	16	640	16	1,300
17	230	17	460	17	900
18	160	18	320	18	640
19	110	19	220	19	450
20	79	20	158	20	320
21	56	21	112	21	220
22	38	22	76	22	160
23	25	23	50	23	110
24	15	24	30	24	77
25	6.8	25	13.6	25	51
				26	30
				27	14

tice now in use is so to manipulate the dilution series that for a given soil sample the portion of the soil material carried forward in each successive dilution is always reduced by one-half. The importance of agitating the suspension thoroughly in every instance while withdrawing the sample for dilution is self-evident. In order to make clear the application of table 3, to studies carried out in this manner, the procedure involved is given in some detail.

Ten grams of the moist soil is suspended in 125 cc. of sterile tap-water by shaking vigorously for 3 minutes; 30 cc. of this suspension is then transferred to a sterile water blank containing 30 cc. of tap-water.

After shaking, this same volume is successively transferred in a similar manner onward throughout the series. The first regular transfer from the original suspension thus gives a dilution of 1:25. However if the dilutions are continued through a complete series of 15 transfers in the manner indicated, the final dilution of the original soil sample will be 1:409, 600. It is readily seen that the extent of the dilution for a given sample will depend upon the comparative density of the population to be measured. For a complete enumeration, it is desirable that the dilutions be carried far enough that some 5 or 6 plates, in a continuous series, remain sterile beyond the last one showing the presence of the organisms concerned. In this connection it should be noted that all sterile plates and not merely those at or near the end of the series are systematically enumerated.

From each of the dilutions of a series so prepared, 1 cc. of the suspension is removed to each of duplicate petri dishes containing sterile nutrient agar. Two or three cubic centimeters of sterile tap-water is then added and the plates incubated. Thus, if the dilution series 1:25–1:102,400 (table 3) is adopted and two plates are inoculated from each dilution inclusively according to the procedure indicated, this will furnish a total of 26 plates for examination. Similarly the series 1:50–1:204,800 and 1:50–1:109,600 will require 26 and 28 plates, respectively.

At the time of examination of any series of plates, the total number of plates actually containing the organism or organisms under observation is determined directly with the microscope. Consequently, the density of the population of a definite species in the original sample may be calculated from the number of positive (or negative) plates in a given series. The number of organisms most closely represented by a given number of negative plates in any of the three series of dilutions mentioned above has been calculated by Mr. Fisher, of the statistical department. These data as originally presented by Cutler (6) are given in table 3.

Thus with a knowledge of the number of sterile plates resulting from the preparation of a definite soil sample in the manner indicated above according to any one of these three dilution series, by proper reference to the table, the number of organisms per gram of original sample which this number of sterile plates represents, can be read off directly. Thus if a sample of soil were prepared according to the dilution interval 1:50–1:204,800, and of the 26 plates thereby provided, 9 were found to be sterile of a particular species, it is seen that of this organism there must be some 7400 per gram in the original sample. The number of organisms per gram of moist soil is then converted to its equivalent value for dry material according to the moisture content of the original sample.

As will be seen, the probable error becomes considerably greater as the number of sterile plates approaches either end of a series. In general, a 2-plate difference has not been regarded as significant. Thus by this method a 12-negative plate result with the 1:50–1:204,800 dilution series would represent 2600 organisms per gram of the original sample but this would not be significantly different from a 10-negative or a 14-negative result. Though the probable error by this method, as is seen, is quite high, the results which it yields are distinctly more accurate and consistent than those obtained by any other developed to the present time.

With regard to the differentiation of the active and cystic forms, a method has been developed whereby the cystic forms are counted directly and the active forms thus determined by difference between total and cystic numbers.

TABLE 4*

Quantitative studies upon the protozoan fauna of some of the soil samples described in table 1

SOIL SAMPLE	FLAGELLATES	CILIATES	AMOEBA
New Jersey 5A	4,320	110	960
New Jersey 5A†	10,314	77	1,482
New Jersey 5B†	6,882	...	3,114
New Jersey 9A	2,773	...	340
Washington	1,508	...	96
Iowa No. 2	1,090	...	140
Texas	891	...	128
South Dakota	417	...	22
Wisconsin	1,889	...	421
Tennessee No. 1 Total	200	...	71
Tennessee No. 1 Cystic	15	...	94
Utah Total	3,180	...	53
Utah Cystic	3,129	...	53

* Only the total numbers are recorded since in stored soils the numbers of active forms will be entirely different from what would obtain in the field. For a complete and accurate enumeration the use of freshly sampled material is absolutely necessary for each group.

† One month later than first plating of 5A.

In the determination of the cystic forms, the dilution method, as outlined above, is used after first treating the soil sample with 2 per cent hydrochloric acid (sp. gr. 1.15) over night. With soils high in lime, it is necessary to determine first the carbonate present so that the acid may be added in such excess that the final strength will be sufficient to accomplish the desired effect. This treatment has been found to destroy effectively all active forms without injuring the cysts.

RESULTS

With one or two exceptions, all quantitative studies have given results that are surprisingly low in comparison with those obtained from Rothamsted soils. Especially is this true of the ciliates which, with one exception, were

not found in any of the plates though the qualitative studies have shown that with one exception, all contain the two more importants pecies of Colpoda noted. Only the total numbers for the general groups will be given, with the exception of the Tennessee and Utah samples where the numbers of cystic forms are noted.

In studying the total numbers of protozoa found in the samples in connection with previous treatment of the soil, one finds, even here, rather marked evidence of the stimulating effect of organic matter. Thus, of the soils of which the previous treatment is definitely known, both 5A and 5B have received liberal applications of cow manure annually (16 tons). The Utah Soil has received 10 tons per year and the Wisconsin soil an average of 4 tons per year. On the other hand, as contrasted with 5A, 9A has received essentially the same treatment but its nitrogen for the past fifteen years has been in the form of sodium nitrate rather than as cow manure. The Tennessee and South Dakota soils, however, have not been fertilized for a considerable number of years.

With regard to cystic forms it was found that the entire population of the Utah soil (previously noted as air dried) appeared to be cystic. In the Tennessee sample, with normal moisture content, only a few of the flagellates were encysted while apparently all of the amoeba were inactive.

No reliance however, can be placed on the proportion of active to cystic forms in these soils, owing to the abnormal conditions produced by their previous storage.

The fluctuations in numbers between the platings of 5A at different periods are of interest in indicating the possibility of periodicity even in these stored soils.

Since these samples of New Jersey soils are quite identical in type and, in the case of 5A and 9A, in treatment, with those studied by Waksman and Starkey (8, p. 137-156) the results here noted may be found to bear directly upon the conclusions drawn by these investigators.

Waksman and Starkey determined (8, p. 250) the presence or absence of the three general groups of Protozoa in a manner essentially qualitative by introducing 1 cc. of a 1:20 dilution of the soil in a medium of known composition and examining after 5 and 14 days. Under these circumstances and with the dilution used, infection by any particular type at the time of examination could in no way define an upper limit to the numbers but would only indicate that there must be more than .5 organism per gram of the original material. On the other hand, sterility in the same instance might define an upper limit to the numbers and indicate that there are probably less than 3-3.5 organisms per gram. Thus in the absence of quantitative values for the protozoa, the conclusion that this group of organisms is inoperative under the conditions studied would seem to be based largely upon the more positive nature and apparently independent activity of the other groups. The observed interactivity of these groups is thus presented as a sufficient explanation, from the biological standpoint, for the phenomena observed.

The results of the present studies presented above might be regarded, in a general way, as supporting the counter-protozoa theory held in common by a number of American workers. Thus the current belief that protozoa do not act as a "limiting factor" in normal American soils, particularly under conditions of partial sterilization, as has been frequently concluded, would not necessarily rest upon a lack of the inherent capacity of these organisms to become a "limiting factor" but rather upon their limited number in the soils studied.

It felt however that until careful studies of freshly sampled soils are made upon a basis similar to that presented in this paper, all conclusions drawn in this connection must be regarded as distinctly tentative.

Sincere gratitude is expressed to Sir John Russell for the privilege of conducting these and other investigations in the Rothamsted laboratory; likewise to Mr. D. W. Cutler under whose immediate direction the present studies were carried out in the protozoological department.

SUMMARY

The examination of a series of soil samples from widely divergent points in the United States shows a considerable uniformity in the distribution of the more important of the three protozoan sub-phyla, Flagellates, Ciliates and Rhizopoda. The range of type genera was found to be quite similar to that holding for English soils.

The results obtained from quantitative studies upon these same samples may be taken to indicate, tentatively at least, that a possible explanation of the difference of the conclusions arrived at by English and American investigators may be found in the difference in the extent of the protozoa fauna in the respective materials investigated. Thus the biological phenomena which follow the partial sterilization of the soil and which have been so extensively studied by both groups of investigators, though admittedly similar in nature, may have as their fundamental basis groups of organisms of quite diverse natures.

In the studies presented, the methods now in use in the Rothamsted Protozoological Laboratory have been applied. For the possible service in further investigations of a similar nature these methods have been briefly described.

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THE INFLUENCE OF SODIUM CHLORIDE UPON ALFALFA GROWN IN SOLUTION CULTURES[1]

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INTRODUCTION

The effects of chlorine salts, especially of sodium chloride, upon plants, have been made the subject of study by a number of investigators since the middle of the nineteenth century.

In one of the early volumes of the Journal of the Royal Agricultural Society of England, there is a report by Hannam (21) to the effect that salt increased both the quantity and the quality of the grain of oats, barley and wheat. Good effects of salt applications are recorded by A. Voelker (78) and, years later by J. A Voelker (80, 81), both, on wheat and on mangels. With this last crop there is a uniformity of favorable reports of the effects of sodium chloride, by a number of investigators, such as Gilchrist (20) and others in England, Christensen (14) in Denmark, and Wheeler and Hartwell (86) in this country. Lawes (39) found no difference in yield of wheat, when comparing plots which received salt with those which did not receive it. With barley, Stewart (69) found sodium chloride to have increased the yield of both the straw and the grain.

Experiments with wheat conducted in this country by Shelton (67) at the Kansas Agricultural Experiment Station, showed some increase in grain and in straw, and the production of a cleaner and brighter straw, with salt applications at the rate of 300 pounds per acre. In a later experiment at the same station (19), with oats, a slight decrease was obtained with 150 pounds of salt per acre. Jones (33), experimenting with salt at the rate of 2000, 3000, 5000 and 10,000 pounds per acre, applied broadcast for the purpose of eradicating weeds, found what he calls the "lighter applications," ultimately beneficial to the grass (meadow fescue). All the weeds were killed with the application of 3000 pounds per acre, while the grass grew larger and was of a darker green than on the non-treated, adjoining field.

Lipman and Davis (41) found that salt up to a concentration of 6000 parts per million, stimulated wheat growth.

Beneficial effects of salt are reported by Bolin (9) in case of oats, hay, kohl-rabi, sugar beets and fodder beets. He attributes it to the chlorine.

Stokes (70) observed carrots to have been benefited by salt applications, especially in dry hot seasons.

Sugar beets are another crop which a number of experimenters found to be benefited by salt applications. Briehm (11), the Department of Agriculture and Technical Instruction in Ireland (16), Strohmer, Briehm and Fallada (72), Mette (44), De Ruijter de Wildt et al (17), Schneidewind, Meyer and Munter (63), Bolin (9), Kruger (38), Hoffman (31), and Tottingham (75), all found increased production when salt was applied. In most cases a greater sugar content was also noticed.

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Walker (84), and also Rudolfs (60) observed an increased yield of asparagus, with salt applications.

Woods (88, 89) reports an increased yield of turnips but not of oats, potatoes or grass, when treated with salt. In his later experiments, however, he observed that with potatoes, the salt gave a small but uniform increase over the untreated plots.

Stood (71) reports, that water containing one gram salt per liter, is harmful to vegetation. Harris (22) considers chloride in soil as the most toxic of the acid radicals, and sodium as the most toxic of the alkalies.

The germination of peas and other legumionous plants, was found by Jarius (32) to be favored by solutions of 0.4 to 1.0 per cent sodium chloride. Hendry (28) found salt had a harmful effect in sand cultures on cowpeas, Mexican garbanzo, and beans.

At the very beginning of the period when attention was directed, by chemists primarily, to the study of the mineral constituents of the plant, a controversy arose as to the relation of chlorine to plant life. Arendt (2) analysed oat plants and found the chlorine content in the ash of the leaves to be less than in that of the stalks; he was not certain whether chlorine was needed or not. Systematic work on this problem was begun by Nobbe and his co-workers (48, 49, 50, 51, 52). They worked with buckwheat in solution cultures, and as a result of repeated experiments, came to the conclusion that chlorine is essential for the growth of that plant and probably also for that of other plants. Leydecker (40), Beyer (6), Birner and Lucanus (8), and Aschoff (4), confirmed the results of Nobbe, and included a number of other plants among those that need chlorine for their best development. Wagner (83) noticed transitory chlorosis in corn grown in a chlorine-free medium, and that no pollen was formed; but he was uncertain whether to ascribe this to the lack of chlorine. Krauch (37) found that sodium chloride was at least not harmtul in solution cultures containing as much as 1 per cent of the salt. Meyer, (45) who made a critical study of the work of the earlier investigators, came to the conclusion that chlorine is needed for buckwheat, but that the quantity needed is very small, and larger amounts may be harmful.

Nobbe's views were opposed most strongly by Knop (35) who denied the essential nature of chlorine in connection with plant growth. Meyer (45), however, pointed out the weakness of Knop's conclusions, mainly on the ground of faulty method in experimentation. Meyer raised the same objections to Aschoff's experiments.

In more recent years, Pfeiffer and Simmermacher (58), who also worked with buckwheat, believe that the existence of a specific need for chlorine has been established, and that the differences of results obtained by the earlier investigators, may be explained by assuming that some plants can do with very little of that element. They show, as Meyer did before them, that buckwheat needs chlorine but in only a very small amount, and may be harmed by larger ones.

The results of a rather extensive investigation by Tottingham (75), show that different plants respond differently to salt treatment: while buckwheat for example, showed a decreased yield, that of carrots and sugar beets was increased. Recent work at the Pennsylvania Agricultural Experiment Station (55) with buckwheat, in washed sand, shows that an increase in dry weight was obtained with salt applications.

Hoagland and Martin (29), working with barley, studied the effect of salts on the intake of inorganic elements and on the buffer system of the plant. From their figures it appears, that with 3000 parts per million of sodium chloride in sand cultures, there was some increase in yield.

The conflicting results obtained in these studies during the last seventy years, and the consequent difference of opinion as to the relation of chlorine salts to plant life, furnish an indication of the complexity of the problem. Some of those investigations, as already pointed out by Meyer (45), suffered from the limitations incident to a lack of knowledge of the proper balance

required to be maintained between the plant nutrients, especially in solution cultures.

Arendt and Knop (3) expressed doubt as to the reliability of the determinations of chlorine in plants. And in fact, it has been repeatedly shown that the analytical data in Wolff's Aschen Analysen, which are of course based upon the earlier determinations, can not always be relied upon, especially with respect to sulfur and chlorine. But even with the improved methods of study at the disposal of investigators to-day, the chlorine question has not reached the stage of definite solution. The effects of sodium chloride, directly and indirectly, in the substratum serving as a medium for plant growth, have been observed to be so multiple and complex, that uniform results should not be expected when different plants or different conditions of the nutrient medium are considered. These effects may be related to the direct action of the salt or its constituent ions, upon plant physiological function; to the action upon other plant nutrients in the medium; to a combination of such activities, as when the sodium of the salt replaces potassium in the plant. The effects may also be related to a physical action exercised by the salt upon the medium, such as the flocculating action on kaolin and on soil noticed by Sachsse and Becker (61).

Nobbe and his associates (48, 49, 50, 51, 52) ascribed to chlorine the rôle of being instrumental in the translocation of starch to the reproductive organs. Meyer (45) concurred in this view but qualified it by saying, that potassium chloride, administered as such, or formed in the salt mixture applied, will perform that function. Aschoff (4) stated that chlorine is probably needed in the building up of each cell. Beyer (6) is of the opinion that chlorine is necessary for seed production.

Interpretations of various kinds have been offered with respect to the effect of sodium chloride on plants grown on soil to which the salt was added. Some of these interpretations are based on observations made upon the behavior of sodium chloride in soil in relation to certain soil constituents or soil conditions.

Voelker (78) explains the good effects of salt applications, as caused by "antiseptic action" which prevents the further decomposition of organic matter and the resulting escape of free ammonia. Peters (56), Frank (18), Eichhorn [cited by Heiden (27)], Beyer (7), Tuxen (76) and Krauch (37), all report, that solutions of sodium chloride extracted a considerably larger amount of mineral and even of organic matter from the soil, than water did. The release of potash was especially noted; but organic matter, sulfur, phosphorus and silica compounds, were also extracted. Eichhorn assumes this to be due to chemical exchange, and suggests that sodium chloride may exchange with soil carbonates, which in turn may act upon even the phosphates of iron and of aluminum, as well as upon the humus. The resulting chlorides of magnesium and of calcium, will again act on the soil, thanks to their pronounced hygroscopic qualities.

Nolte (53) also found that sodium chloride increased the amount of nitrogen, potash and lime in the soil percolate.

From the work of Wheeler (85), Wheeler and Adams (86), Wheeler and Hartwell (87), Hartwell, Wheeler and Pember (24), and Hartwell and Damon (25), which relates to investigations with sodium chloride begun at the Rhode Island Station in 1894 and which was still going on in 1919, it has been established that with some plants, such as beets, radishes, turnips and carrots, sodium can in part take the place of potassium. Increased yield, increased percentage of sodium accompanied by a decreased percentage of potassium, and consequently a better utilization of this element, was brought about by salt applications. Their work also indicates that sodium chloride tends to liberate phosphorus and potassium, and that salt applications may prove of benefit even when full rations of potash are supplied.

Mitscherlich (46) recently asserted that sodium compounds will hinder the formation of difficultly soluble potash compounds in the soil, and thus cause a better utilization of potassium by the plant. Schultze (65, 66) maintains that sodium chloride does not release potassium from potash-zeolites. The plants, according to him, use the sodium as a nutrient, since it may replace potassium to a certain extent. Atterberg (5) experimenting with oats, also comes to the conclusion, that the sodium in sodium chloride may partially replace potassium in the plant. Stood (71) noticed that an increased sodium content is accompanied by a reduction in potash, which fact would likewise indicate a partial replacement of the latter by the former. Suchting (74) similarly noted a depression of the potassium content of potatoes, which received applications of sodium salts. Markwort (43) found that in the case of the sugar beet, sodium applied to the soil, migrates almost completely to the leaves and reduces their potash requirement, thus making available a larger amount for other parts of the plant.

Hoffman (31) found that common salt increased both the quantity and quality of sugar beets, on light as well as on heavy soils, when applications of potash were light and those of sodium chloride heavy. Breazeale (10) observed that plants which have been growing for a period in a medium containing sodium, took up less potash when later transferred to a medium supplied with this element, than did plants which have been growing in a solution containing no sodium.

Voelker (79), and also Kruger (38) are of the opinion that sodium can not replace potassium. In Christensen's (14) experiments, salt caused an increase in the percentage of potassium; he therefore concludes that salt does not assume partly the rôle of potash applications. The chlorine intake was increased more than that of sodium in case of mangolds, and the chlorine, according to him, plays an important part. With potatoes, the salt acted unfavorably, and the chlorine content was increased while that of sodium was not.

Tottingham (75) likewise assumes chlorine to be the active element, and that sodium chloride may act directly as a fertilizer.

In the case of sand cultures, a larger amount of potash was taken up by the barley in the experiments of Hoagland and Martin (29), when sodium chloride was applied at the rate of 3000 parts per million. There was a somewhat greater yield and also a greater percentage of potash in the plants.

Birner and Lucanus (8) state that sodium chloride retards the intake by the plant of lime, sulfur and phosphoric acid, and that it increases the dry matter (in oats) and the quantity of potash and magnesia in the ash.

If the action of sodium chloride in the soil is due to the power of the salt of releasing needed nutrients for the plants, the failure to show any gains with salt applications reported by Lawes (39), may possibly be due to the fact that he applied at the same time an abundance of fertilizers; the salt would in such a case not have an opportunity to assert its effect.

Mette (44) believes the beneficial effects of sodium chloride noted by him, were due to the hygroscopic action of the salt during dry weather.

Den Berger (15) found that sodium chloride may cause puddling, a breaking down of zeolitic materials and changes in volume of soil colloids. Haselhoff (26) also observed chlorides to have injuriously affected the physical composition of the soil, especially that of the loam or clay type. Nolte (53), on the other hand, reports that sodium chloride, the same as sodium nitrate and sodium sulfate, increased the permeability of the soil. Kossovich (36) noted that the sodium chloride hastened the rise of water in a loess clay soil.

Some investigators ascribe the so often noticed superiority of sodium nitrate over ammonium sulfate in fertilizer experiments and practice, as due to the sodium. Schulze (64) found that even in a heavy soil, sodium chloride increased the effect of ammonium sulfate. Briehm (12), also Strohmer and Fallada (73) report that with sugar beets, as good effects were obtained when sodium chloride was applied in combination with ammonium sulfate, as when sodium nitrate alone was applied. Soderbaum (68) however, noticed a benefit with sodium chloride, whether in combination with amonium sulfate or with sodium nitrate, but

not with ammonium chloride. He therefore attributes the good effects to the chlorine. Von Feilitzen (82) could notice no effect of sodium chloride when added to ammonium sulfate. But since he worked with peat soils, it is possible that acidity was a limiting factor, in which case sodium nitrate should prove of greater benefit.

According to Osterhout (54), sodium chloride ions readily penetrate the protoplasm. Reed and Haas (59) present data showing that sodium and chlorine are not absorbed from a sodium chloride solution, as molecular NaCl, but as sodium ions and chloride ions. Christensen, (14) as noted previously, found that the chlorine intake was increased more than that of sodium.

Chittenden and Wachsman (13) state that the activity of diastase is enhanced in the presence of small amounts of sodium chloride.

With wheat in nutrient solutions, Pethybridge (57) observed the leaves to become thinner and to be of a darker green on addition of sodium chloride. Harter (23), also working with wheat plants, reports, that in a soil containing 0.7 to 1.4 per cent sodium chloride, even if given sufficient water, the plants will immediately after germination assume xerophytic characters. There was a deposit of a waxy bloom on the leaf surface, and a thickening of the cuticle, both of which features tend to lessen transpiration. An increased concentration of the cell sap also took place. When the amount of salt present was not sufficient to cause alteration of structure (with concentrations of 0.06 to 0.08 per cent of sodium chloride in the soil), the transpiration was even increased. Breazeale (10) noticed increased transpiration in presence of sodium even when potash and other minerals were supplied in abundance.

Van Hecke (77) experimenting with fruit trees, found that trees which received 3 pounds of salt were free from gummosis, while the check trees were seriously damaged. He refers to observations made by DeGreffin in Zealand, and by Heime in China, that some fruit trees grown in a soil rich in sodium chloride, did not suffer from gummosis.

Hoffmann (30) studied various salt plants in their relation to sodium chloride, and reported that some sea plants, like *Plantago maritima*, may grow without salt, and that it is only a matter of greater tolerance and not of need, for sodium chloride. The sodium chloride of salt plants may be replaced by potassium chloride. Certain plants, like *Crambe maritima*, show an increased proportion of potassium to sodium, as the distance from the shore, of the locality where they grow, increases. Schimper (62) on the other hand states, that phanerogams which usually live at the sea shore, maintain their chlorophilous habit even when grown on ordinary soil. He also states, that in the case of shore plants, the chlorine is present mostly as sodium chloride, while if grown in places poorer in chlorine, it is mainly in the form of potassium chloride and found chiefly in the leaves.

Jung (34) made up a list of numerous plants which he divides into chlorophilous groups and chlorophobous ones. Leguminosae are not given in any of those groups.

OBJECT OF EXPERIMENT

In a paper published by the writer (42) recently, references was made to the varying chlorine content of alfalfa, and there were also presented the results of an experiment with water cultures that brought out some relationships of that plant to sodium chloride applications. The present investigation comprises a more detailed study of the subject. A greater range of sodium chloride concentrations is covered, the total concentration of the solutions was different from the one used in the previous study, additional phases, such as water absorption and water requirements, were investigated; some details of the experiment were carried out in what might be considered an improved manner, and pot experiments with soil (which will be reported in a separate paper) were also included.

METHOD OF PROCEDURE

Alfalfa seed of the lot used in the previous experiments (42), was used throughout the present work. For germination, the seeds were placed in a spacious crystallizing dish lined with blotting paper, and kept moist with solution "IR2S1." (47), diluted ten times. On August 20, 1923, two days after sowing, the seedlings were transferred to the germinating net. This consisted of thinly paraffined mosquito bar stretched tautly over the top of an "agateware" pan, 12 inches upper diameter and 3 inches high. A double net was used. After the first net was fastened around the pan, a square made of glass rodding 5 mm. in diameter, and reaching almost to the rim of the pan, was laid over it; another net, made up of two thicknesses of mosquito bar, was stretched over the first, the two nets being separated from one another by the thickness of the glass rodding. The two layers of mosquito bar making up the upper net, were laid together in such a way that the meshes of the one were cut by the threads of the other, thus reducing the size of the meshes of both layers forming the upper net. This prevented the seedlings from slipping through.

On August 29 the plantlets were tranferred to the jars containing the corresponding solutions, three plants to a jar. Since duplicate jars were run for each culture, there were six plants for any particular culture solution. The checks were run in triplicates, giving nine plants for this culture.

The solution known as "R5C2" (Shive), of osmotic value of 1.75 atmospheres, found satisfactory for wheat, and given by the National Research Council (47) as universal control culture in solution culture studies, was here used as check. The solutions to which sodium chloride was added, were derived from this one, by maintaining in each case the total concentration of the solution as a whole, and the proportions of the three salts, KH_2PO_4, $Ca(NO_3)_2$ and $MgSO_4$, the same as in the check, but substituting sodium chloride, in increments of 0.1 atmosphere, in place of a corresponding osmotic value of the other three salts combined. This reduction in the osmotic value of the original three salts, was distributed in such a manner, as to leave their initial osmotic proportion undisturbed, varying only their total combined concentration.

In the present work it was thought preferable to proceed in this way rather than by superimposing the new salt or substituting it for one present in the check. Superimposing increases the total concentration; substituting the new salt for one present in the check, even when done in osmotic equivalents, disturbs the proportion of the original salts present. In a solution like that of the present check with a total osmotic concentration of the fairly high value of 1.75 atmospheres, less significant change is likely to be introduced into the medium aside from that caused by the new factor to be studied. Only the total combined concentration of the original salts is lessened, while the proportions in which they are present in the check and the initial total concentration of the solution are maintained.

The respective values of the different solutions used, are given in table 1.

The solutions were renewed every three and one-half days at which time measurements of water absorption were also made; these constituted the partial measurements which at the end were added up to give the total, and from which the water requirements were computed.

Chemically pure salts were used to make up the 0.5 *M* stock solutions from which the culture solutions were prepared. The sodium chloride was dried to constant weight before being weighed out for the making up of the stock solution.

Iron was supplied in the form of "soluble ferric phosphate," which was made up into a solution containing approximately 0.5 mgm. per cc.. A few drops of this solution were added each time the culture solutions were renewed.

TABLE 1

Partial volume-molecular concentrations and partial osmotic concentrations (in atmospheres), of KH_2PO_4, $Ca(NO_3)_2$, $MgSO_4$ and NaCl; also osmotic proportions of KH_2PO_4, $Ca(NO_3)_2$ and $MgSO_4$, in solutions used for the study of the effect of sodium chloride

SOLUTION NUMBER	PARTIAL CONCENTRATIONS							
	Volume—molecular				Osmotic (atmospheres)*			
	KH_2PO_4	$Ca(NO_3)_2$	$MgSO_4$	NaCl	KH_2PO_4	$Ca(NO_3)_2$	$MgSO_4$	NaCl
Check	0.01800	0.0052	0.0150	0.0000	0.875	0.350	0.525	0.000
1	0.01697	0.0049	0.0142	0.00188	0.825	0.330	0.495	0.100
2	0.01594	0.0046	0.0134	0.00376	0.775	0.310	0.465	0.200
3	0.01491	0.0043	0.0126	0.00564	0.725	0.290	0.435	0.300
4	0.01388	0.0040	0.0118	0.00752	0.675	0.270	0.405	0.400
5	0.01285	0.0047	0.0110	0.00940	0.625	0.250	0.375	0.500
6	0.01182	0.0034	0.0102	0.01128	0.575	0.230	0.345	0.600

*In each solution the osmotic proportions of the original three salts are as 5:2:3.

The plants were grown in quart jars for 77 days, and were harvested on November 14, 1923; the tops were separated from the roots at the crown; the drying was done at the temperature of boiling water for 24 hours, at the end of which, the tops and the roots from each jar were weighed separately.

The tops and roots of each jar were ground and analysed separately; the methods of analysis followed, were those of the Association of Official Agricultural Chemists (1).

DISCUSSION OF RESULTS

The data on yield, water absorption, water requirements, nitrogen and chlorine content, are presented separately for tops, roots and for whole plants, in table 2 and in figure 1.

Considering the total yield, in tops and roots combined, it is seen that an increase amounting to 47 per cent over the check taken as 100, was obtained with solution 5, which contained 0.5 atmosphere sodium chloride. An even

TABLE 2

Effect of sodium chloride on yield, water absorption, water requirements, nitrogen and chlorine content of alfalfa grown in solution cultures; average of duplicate cultures; check, average of triplicates

		CHECK SOLUTION: atmos. NaCl....0.00 KH_2PO_4...0.875 $Ca(NO_3)_2$..0.350 $MgSO_4$....0.525	SOLUTION 1: atmos. NaCl....0.100 KH_2PO_4...0.825 $Ca(NO_3)_2$..0.330 $MgSO_4$....0.495	SOLUTION 2: atmos. NaCl....0.200 KH_2PO_4...0.775 $Ca(NO_3)_2$..0.310 $MgSO_4$....0.465	SOLUTION 3: atmos. NaCl....0.300 KH_2PO_4...0.725 $Ca(NO_3)_2$..0.290 $MgSO_4$....0.435	SOLUTION 4: atmos. NaCl....0.400 KH_2PO_4...0.675 $Ca(NO_3)_2$..0.270 $MgSO_4$....0.405	SOLUTION 5: atmos. NaCl....0.500 KH_2PO_4...0.625 $Ca(NO_3)_2$..0.250 $MgSO_4$....0.375	SOLUTION 6: atmos. NaCl....0.600 KH_2PO_4...0.575 $Ca(NO_3)_2$..0.230 $MgSO_4$....0.345
Dry weight, *grams*	Tops	3.895	4.499	3.849	4.826	3.238	6.208	4.797
	Roots	1.352	1.534	1.337	1.583	1.247	1.545	1.393
	Whole plants	5.247	6.033	5.186	6.409	4.485	7.753	6.190
Relative dry weights	Tops	100.00	115.51	98.82	123.9	83.1	159.4	123.2
	Roots	100.00	113.46	98.89	117.0	92.2	114.3	103.0
	Whole plants	100.00	114.99	98.84	122.1	85.5	147.8	117.9
Water absorption, *cc.*		2,227	2,532	2,208	2,659	1,993	3,283	2,546
Water requirement, *cc.*	Tops	576.6	562.0	574.0	556.8	622.3	529.9	544.2
	Roots	1,652.6	1,643.0	1,674.2	1,625.0	1,598.0	2,117.0	1,839.0
	Whole plants	426.6	418.6	426.8	412.2	447.3	421.9	419.5
Nitrogen content, *per cent*	Tops	3.38	3.45	3.15	3.29	3.52	3.18	3.43
	Roots	3.03	2.75	2.50	3.02	2.56	2.80	2.89
	Whole plants	3.29	3.27	2.98	3.21	3.25	3.10	3.31
Chlorine content, *per cent*	Tops	0.04	0.21	0.36	0.37	0.66	0.63	0.80
	Roots	0.04	0.18	0.24	0.29	0.43	0.53	0.86
	Whole plants	0.04	0.20	0.33	0.35	0.60	0.61	0.81

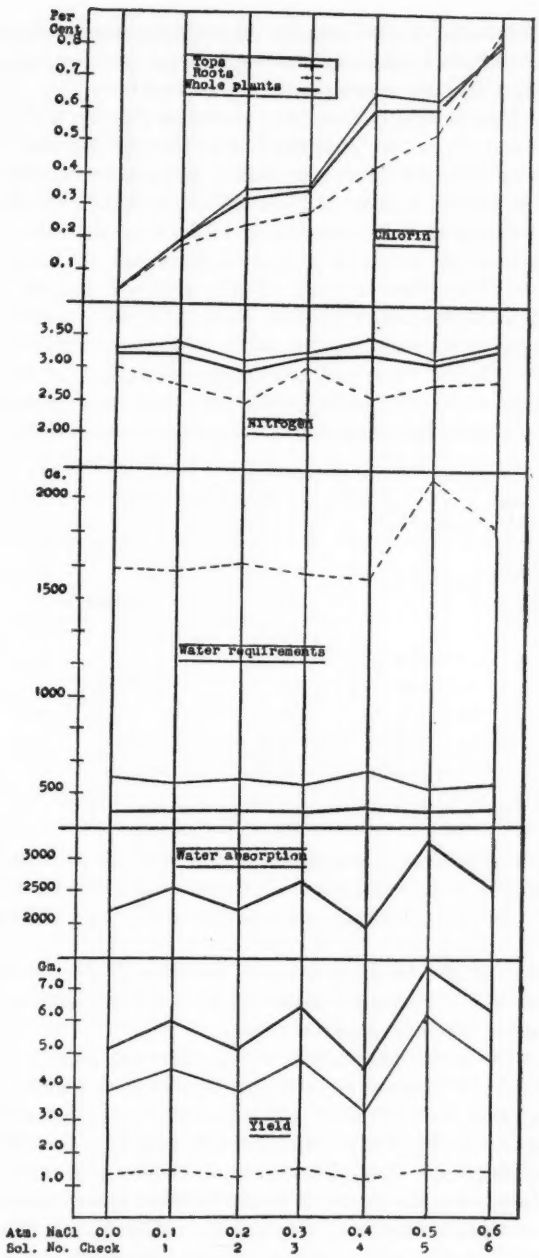

FIG. 1. GRAPHIC SUMMARY OF DATA DETERMINED

higher relative increase of tops, namely, 59 per cent, was produced by this solution. The relative increase in roots was 14 per cent, which is slightly below the highest relative increase in roots produced by solution 3, with 0.3 atmosphere sodium chloride. Solution 3 produced the next highest relative increases, 23.9 and 22 per cent of tops and whole plants, respectively, over the corresponding values of the check. Solution 6, which received 0.6 atmosphere sodium chloride, is third in order of increase over check with respect to whole plant yield, the value of this increase being 18 per cent; the value for the increase in tops, however, is substantially the same as that of solution 3. Solution 1, with 0.1 atmosphere sodium chloride, produced a relative increase over the check of 15 per cent each for tops and whole plants, and a somewhat slighter increase, 13 per cent, for the roots. Solution 2, with 0.2 atmosphere sodium chloride, showed a slight relative decrease of about 1 per cent for tops, roots and whole plants, as compared with the check. A significant relative decrease was shown by one solution out of the six containing sodium chloride.

TABLE 3

Comparison of values for water absorption in relation to yield of whole plant found, with those calculated on the basis of water absorption relative to yield of whole plant of check

SOLUTION NUMBER	YIELD (WHOLE PLANT)	WATER ABSORPTION		DIFFERENCE
		Found	Calculated	
		cc.	*cc.*	*per cent*
Check	100.0	2,227		
1	115.0	2,532	2,560	−1.1
2	98.8	2,208	2,200	−0.4
3	122.1	2,659	2,719	−2.2
4	85.5	1,993	1,904	+4.5
5	147.8	3,283	3,291	−0.3
6	117.9	2,546	2,625	−3.0

This was solution 4, with 0.4 atmosphere of that salt. In this case, the values for tops, roots and whole plants, as compared with the check taken as 100, were 83, 92 and 85 respctively, a relative decrease for the whole plant of 15 per cent.

The greatest relative increases occurred in the yield of tops; this is worth nothing, since in the literature dealing with this subject it is often emphasized that the roots are affected to a great extent.

The curve for water absorption, it will be observed, follows the direction of those for yields of tops and whole plant. The greatest quantity of water absorbed, took place from culture 5, which produced the greatest yield. The water absorption by the plants in the other solutions, followed closely the order of yield of whole plant. This is brought out more clearly in table 3 in which, for comparison, are given the actual figures for water absorption by the plants in the different solutions and a corresponding set of figures calculated by using the yield of whole plant and water absorption of the check as a basis. From

the column giving the differences, in per cent, between the amount calculated and the amount found, a very close approximation is shown to exist between the two sets of figures. It would therefore seem, that with solutions of the type here used, water absorption is a direct function of yield of whole plant for alfalfa, at least during the first 11 weeks.

The values for water requirements, do not show much variation, if whole plant yields are considered. This was to be expected, after the relationship which has just been shown to exist between water absorption and yield of whole plant. It is only with solution 4, which produced the lowest yield, that the water requirement runs up to 447 cc., as against 426 cc. of the check. The differences between the other cultures, expressed in per cent, and the check, range from 0.0 to 3.5. When comparison is made between the water requirements for the yields of tops of the different solutions, more pronounced differences are encountered. Here we find the lowest value, 530, for solution 5 which produced the highest top yield, and the highest value, 622, for solution 4, with the lowest yield of tops. The reverse relationship applies to the roots of these respective solutions, the values being 2117 and 1598 for solutions 5 and 4, respectively. This would indicate, that where the total yield was low the ratio of root growth to that of tops, was greater than where the total yield was high. In the two extreme cases of cultures 4 and 5 which respectively represent the lowest and highest yield, the root yields were respectively 28 and 20 per cent of the total.

The percentages of nitrogen in the plant as a whole, do not show variations of a magnitude to indicate any definite relationship between this criterion and that of any of the others studied. In all solutions except solution 3, the roots show a larger percentage of nitrogen than that present in the roots of the plants from the check culture. Of the nitrogen percentage in tops, culture 5, with the highest yield, gave tops with a value of 3.18, substantially the same as the lowest value for nitrogen percentage of tops in any of the seven cultures studied. Culture 4, with the lowest yield, contained 3.52 per cent nitrogen in tops, which was the highest value for any of the seven cultures. But, considered in the light of the usually prevalent variations in the nitrogen content of even the same kind of plants grown under what appears to be the same conditions, the differences here noted cannot, without further investigation be taken to indicate the existence of a clearly defined relationship between the the nitrogen content and any other criterion of growth here considered.

In the previous preliminary study (42) on the effect of sodium chloride on alfalfa referred to, it was found that the chlorine intake of the plant in the different solutions, varied directly with the amount of sodium chloride supplied, and that this held good for the roots as well as for the tops. The roots, however, had a considerably smaller percentage of chlorine than the tops. Similar results were obtained in the present study up the limit of the range of sodium chloride applications tested. And since the range here covered was 0.2 atmosphere higher than the one previously studied, and considering further that the

total concentration of the solutions in the present investigation was 1.75 atmospheres, or 0.75 atmosphere higher than the total concentration previously used, it would seem justifiable to conclude from the similarity of results obtained under the two different conditions that alfalfa in solution cultures supplied with sodium chloride, will, within the limits tested, take up an increasingly larger amount of chlorine with the amount of sodium chloride supplied.

With respect to yields, the results of the present study likewise approach those obtained in the earlier one: an increase in yield usually being produced by the solutions containing sodium chloride.

The observation made in connection with the previous study, that no evidence was found of any relationship between the nitrogen content of the plants from the different solutions, and any other criteria of plant measurements, was found to apply also to the results obtained in the present study.

There is likely to be difference of opinion as to whether, in consideration of the fact that the sodium chloride also caused yield increases, the salt acts as a stimulant or as a mineral nutrient for the alfalfa plant. As yet no well defined distinction has been established between the terms "stimulant" and nutrient." It would appear, however, that the term "stimulant," in connection with chemical elements taken up by the plant, should be restricted to denote a substance which, when present in the medium, enhances growth without necessarily being absorbed by the plant in any significant quantity. At any rate, the amount taken up may not at all bear a direct relation to that supplied. With such tentative distinction in mind, and making due allowance for the various effects that sodium chloride may exercise when applied to the soil, it may not be improper to assume, that the sodium chloride here supplied to the alfalfa in solution cultures, acted as a mineral nutrient, which helped materially towards a better development of the plant.

SUMMARY AND CONCLUSIONS

1. Alfalfa was grown for 77 days in solutions with amounts of sodium chloride varying from 0.0 to 0.6 atmosphere osmotic pressure; Shive's solutions R5C2 (1.75 atm.) being used as check.

2. An increase in yield over the check was observed in five out of the six cultures containing sodium chloride.

3. The greatest relative increase occurred in the yield of tops.

4. The curve for water absorption followed the direction of the curves for yields of tops and for those of whole plants.

5. Not much variation was noticed in the values for water requirement, when whole plant yields are considered.

6. More pronounced differences were found when the values for the water requirements of tops are compared. The lowest value, 530 corresponds to the cultures with the highest top yield, while the highest value, 622, resulted with the culture producing the lowest yield of tops.

7. There is an indication, that the ratio of root growth to that of tops, is greater where total yield was low than where total yield was high.

8. The variations in the nitrogen percentages of the whole plants, were not of an order to indicate with certainty any definite relationship between this datum and any of the others studied. The roots from the sodium chloride cultures show a larger nitrogen percentage than those from the check cultures.

9. The chlorine intake of the plants varied directly with the amount of sodium chloride supplied. This applies to the roots as well as to the tops. The roots however containing a much smaller percentage than the tops.

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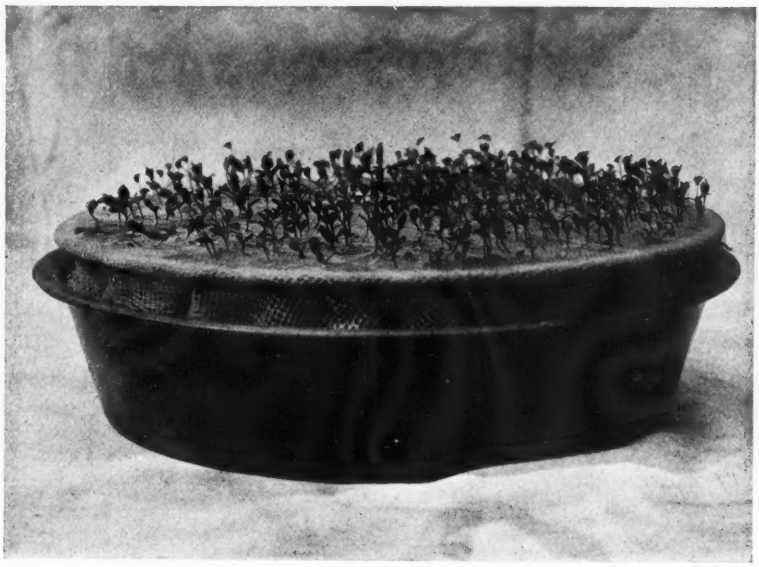

PHOTO SHOWING THE METHOD OF GROWING ALFALFA SEEDLINGS

NOTES ON A METHOD FOR THE DETERMINATION OF SULFUR IN SOIL

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Within recent years, the question of sulfur as a factor in soil fertility has assumed considerable importance. With the growth of interest in the question, several experiment stations have made sulfur determinations of their soils. Strangely enough up to the present time, there has been no satisfactory method for the purpose. The so-called "official" method of the Association of Official Agricultural Chemists, as adopted in 1907 (4) was recently taken off the "official" list, and placed into the "tentative" class (5). Realizing that the method was very unsatisfactory, the Association in 1919 appointed a referee on methods for the determination of sulfur in soils. The referee reported on his work in 1920 (1) and again in 1921 (2).

Notwithstanding the considerable amount of work done by the referee and his associates in coöperation with various experiment stations, the method thus evolved failed to satisfy the referee, who recommends a further study of methods. Six different methods of bringing the sulfur into soluble form were studied by the referee; viz. (1) sodium peroxide combustion, (2) magnesium nitrate combustion, (3) aqua regia digestion, (4) nitric acid digestion, (5) combustion with a mixture of magnesium nitrate, calcium carbonate, and ammonium chloride, and (6) calcium peroxide combustion.

In every one of these methods, soil charges of 10 to 25 gm. were used. Correspondingly large amounts of reagents had to be used, which in turn necessitated the employment of large-sized glassware. All this makes the methods rather cumbersome and time consuming.

Previous to precipitation of the sulfur, iron and aluminum are precipitated, which operation introduces a very undesirable feature. Precipitates iron and aluminum hydroxides have a large capacity for absorption of sulfates, and successful washing of sulfates from these hydroxides is an exceedingly difficult task.

OLSON'S METHOD OF SULFUR DETERMINATION IN SOIL

In the evolution of a method for sulfur determination in soils, the Olson's modification (3) is a step in the right direction. The Olson's method (3, p. 7-11), in substance, is as follows:

Two grams of soil, 10 to 12 gm. sodium peroxide, 0.5 gm. sugar, and 1 gm. of a finely ground mixture consisting of 5 parts of boric acid, 4 parts of sodium nitrate, and 1 part of metallic magnesium, are placed in a Parr electric sulfur bomb. The ingredients are thoroughly mixed, and the charge is exploded with the bomb under water. The charge is taken up with water or acid, and dehydrated from one to three times to remove silica. The precipitation with barium chloride is made in the cold and in the presence of iron and aluminum. Olson states (3, p 9) that it was found preferable to "add 10 cc. of 10 per cent cold barium chloride slowly and evenly on the surface of cold liquid, which has first been neutralized with ammonium hydroxide and then slightly acidified with from five to six drops of concentrated HCl. Upon standing twelve or more hours, the mixture of sulfates and barium chloride is thoroughly stirred, after which it is allowed to stand at least until the barium sulfate has nearly, if not entirely, settled.

Olson's method has several distinct advantages in comparison with the old procedure adhered to by the Association of Official Agricultural Chemists, or those recently proposed by its referee. In the first place, in precipitating sulfur in the presence of iron and aluminum, it avoids the danger of losing some sulfur in absorption by iron hydroxide. In the second place, it deals with a small amount of soil, thus permitting the operation to be carried out in smaller containers. This point, however, is carried too far for the best results. In the third place, in exploding the soil mass in the Parr's bomb, the disintegration of soil and oxidation of sulfur are unquestionably complete.

A PROPOSED MODIFICATION OF METHOD FOR SULFUR DETERMINATION IN SOIL

In taking up the systematic sulfur determination of Illinois soils in connection with the soil survey of the state, several methods were tried in this laboratory. A modification of Olson's method was finally adopted that with three years of usage has proved to be shortest in operation and among the most reliable in the results obtained, as compared with any method that has come under the writer's observation.[1] This modification allows the use of a somewhat larger soil sample, permits employment of a simpler and less expensive bomb for the disintegration of the soil, simplifies the accelerating agent, and shortens the procedure by eliminating a second dehydration of silica and by making a neutralization by ammonia unnecessary.

The modification, as adopted in this laboratory, is presented herewith:

Three grams of soil (0.5–1.5 gm. of peat or muck) are mixed with 0.5 gm. of powdered magnesium (to start the combustion) and 10 to 15 gm. of sodium peroxide in a Parr heat ignition bomb. The bomb is closed, and the contents are exploded by heating the bomb moderately over the free flame of a Bunsen burner. The bomb is cooled by setting it in cold running water, covering three-fourths of its height. The fusion is washed with hot water from the bomb into a 400-cc. beaker, neutralized with 1:1 HCl; an excess of HCl is added and the solution evaporated on a water or steam bath until the silica is thoroughly dehydrated. From 24 to 48 hours is usually required for evaporation and drying. The residue is taken up with 10 or 15 cc. 1:1 HCl, the beaker is covered with a watch glass, and

[1] The writer wishes to acknowledge his sincere appreciation of Mr. George Van der Veer's assistance in developing the method.

heated on a steam bath for 5 or 10 minutes. The moistened material is diluted with about 100 cc. hot water, washing the sides of the beaker and stirring the mass of material. The hydration is continued for another 5 or 10 minutes. The solution is then filtered through an 11-cm. Whatman's no. 4 filter paper, or any other suitable paper, and washed with hot water until nearly free from chlorides. The filtrate, which amounts to 200 or 250 cc. is heated to boiling, and sulfur is precipitated with 10 cc. of a 10 per cent solution of $BaCl_2$, and allowed to stand for 24 hours with occasional stirring. The precipitate is slow in forming and for this reason the standing for two days is sometimes desirable. The precipitate is filtered on a previously weighed Gooch crucible with the use of a substantial mat of long fiber asbestos and moderate suction. The precipitate should be washed five or six times with hot water, dried and the contents ignited in the Gooch crucible at a low temperature. The crucible is cooled in a desiccator and weighed. The percentage of sulfur in the barium sulfate is 13.7343.

The sulfur content of the reagents should be determined, and subtracted from that found in the soil. The blank can be determined either by a direct analysis of the reagents or by determining the sulfur in two different amounts of the same soil. A convenient ratio of one amount to another is 2 to 1, or 3 gm. and 1.5 gm. of soil. Then, twice the amount of sulfur in 1.5 gm. minus the amount obtained from 3 gm. will give the amount of sulfur contained in the reagents. Or,

$$2(a + x) - (2a + x) = x.$$

when x = amount of sulfur in reagents, and a = amount of sulfur in 1.5 gm of soil.

In using ten Parr ignition bombs, which may constitute a set, and three frames for the bombs, one can conduct the explosions nearly as fast as one can make fusions in open iron crucibles, the difference in the time consumed being due to closing the bombs before and opening after the explosion. With one bomb in water for cooling after the explosion, another one on the Bunsen burner, and a third in preparation for heating, one's time will be completely occupied during this part of the process.

EXPERIMENTAL

In offering the above procedure of sulfur determination in soils, it is felt that there is considerable justification for every step in the proposed outline. The soil charge was increased from 2 to 3 grams in order to allow the precipitation of a larger amount of sulfur, which is of considerable advantage in as much as the sulfur content in soils is ordinarily very low.

Granulated magnesium metal, is a very good accelerator of the reaction, and is usually fairly free from sulfur. Some preliminary work showed that about 0.5 gm. of granulated magnesium is the right amount to use with 3 gm. of soil and 10 to 15 gm. of sodium peroxide. A smaller amount of magnesium retards the reaction, making it difficult to notice the explosion. Larger amounts of magnesium, on the other hand, cause the reaction to proceed so violently that bursting of the bomb may result. Ten or twelve grams of sodium per-

oxide were found to be sufficient with an ordinary charge of soil. Larger amounts of peroxide cause an increase in the salt content of the resultant solution, which makes the subsequent precipitation of sulfates difficult.

Amount of hydrochloric acid to use

In taking up the dehydrated mass, 10 or 15 cc. of 1 : 1 HCl is sufficient. When the dehydrated mass is taken up with this small amount of hydrochloric acid, the sulfur may be precipitated without neutralizing the acidity of the resultant solution, as may be judged from the results of an experiment presented in table 1. In this experiment, samples of the same soil were so treated that a difference in the acidity present existed at the time of the precipitation of the sulfur. Table 1 is self-explanatory. The averages of two

TABLE 1

Effect of the degree of acidity of the solution upon the amount of $BaSO_4$ obtained in sulfur determinations

	TREATMENT OF SOLUTION BEFORE PRECIPITATING SULFUR	AMOUNT $BaSO_4$ OBTAINED
		gm.
1	10 cc. 1:1 HCl used in taking up material after dehydrating silica	0.0120
2	15 cc. of 1:1 HCl used in taking up material after dehydrating silica	0.0114
3	Same as (2) plus 15 cc. 1:1 HCl just before precipitation of sulfur	0.0107
4	Same as (2) plus 30 cc. 1:1 HCl just before precipitation of sulfur	0.0098
5	Same as (2) plus 30 cc. concentrated HCl just before precipitation of sulfur	0.0034
6	Same as (1) plus 2.5 cc. concentrated ammonia to nearly neutralize the acidity of the solution	0.0115

determinations are given in all the tables. The results show that samples with treatments of 10 and 15 cc. of 1 : 1 HCl, as well as those in which the resultant solution was neutralized, gave practically the same amounts of $BaSO_4$ in the precipitate, the respective figures being 0.0120, 0.0114, and 0.0115 gm. $BaSO_4$. With the increase in acidity of solution before the precipitation of the sulfates, the amount of $BaSO_4$ was proportionally decreased.

It may be noticed in passing that, when 10 or 15 cc. 1 : 1 HCl are added to the dehydrated mass, the effective acidity due to this acid is very materially decreased by evaporation on heating, and also by the buffer action of various salts in solution. The trials show that less than 3 cc. of strong ammonia water is sufficient to neutralize the acid present in the resultant solution in which a dedydrated material was treated with 10 cc. 1 : 1 HCl. A larger amount of added HCl would lose proportionally a large percentage of its effective acidity.

Iron and aluminum should not be removed

The question of whether or not to precipitate iron, aluminum, etc., before precipitating sulfur, deserves special attention since precipitated iron has a large capacity for absorbing the sulfates. A complete washing of sulfates from hydroxide is a very difficult task. The following experiment throws some light on the subject.

Two soils were treated with $CaSO_4$ before fusion with sodium peroxide. After the fusion sulfur was determined in these soils in the presence of iron and aluminum, and also after iron and aluminum were removed by a double precipitation with ammonium hydroxide. The combined filtrates amounting to 400 cc. were reduced to about 200 cc. by evaporation, and the sulfur precipitated as in the samples where iron and aluminum were not removed. The results are presented in table 2. They show that all the added sulfur was ob-

TABLE 2

Effect of iron and aluminum precipitation on sulfur determination and sulfur recovery; amount of $BaSO_4$ obtained from soils treated or untreated with $CaSO_4$, and also from $CaSO_4$ solution

SOIL NUMBER	TREATMENT	PRECIPITATED IN PRESENCE OF IRON AND ALUMINUM		IRON AND ALUMINUM REMOVED BEFORE SULFATES WERE PRECIPITATED	
		As determined in soil	$BaSO_4$ due to sulfur added as $CaSO_4$	As determined in soil	$BaSO_4$ due to sulfur added as $CaSO_4$
		gm.	*gm.*	*gm.*	*gm.*
S3286	Untreated	0.0119		0.0068	
S3286	0.05 gm. $CaSO_4$	0.0935	0.0816	0.0654	0.0586
5133	Untreated	0.0050		0.0025	
5133	0.05 gm. $CaSO_4$	0.0859	0.0809	0.0644	0.0619
0.05 gm. of $CaSO_4$ (no soil)			0.0808		0.0808

tained (after subtracting the amount found in the untreated soil) in samples where iron and aluminum were not removed. On the other hand, when iron and aluminum were removed, there was a considerable amount of sulfur lost in both the treated and untreated soils. It would seem, therefore, that, unless one is very careful to remove all sulfates from the iron and aluminum precipitate, it would be a dangerous procedure to remove iron and aluminum by precipitating them with ammonia. Perhaps other means of precipitating iron and aluminum are less dangerous for a sulfur determination. The removal of iron and aluminum is unnecessary, since iron, aluminum, or mixtures of the two elements have no effect on sulfur determination, when these elements are present in the form of chlorides. The following experiment confirms this view.

Portions of an ammonium sulfate solution, containing 0.05 gm. ammonium sulfate, were treated with a solution of $FeCl_3$, $AlCl_3$, or with a mixture of

the two salts, each portion containing 0.2 gm. of salt. After dilution, the sulfates were precipitated and the sulfur determined. The results are presented in table 3. They show that iron and aluminum present in solution did not reduce to any considerable extent the amount of sulfur obtained as $BaSO_4$.

The results obtained in this experiment, as well as those in the preceeding experiment, show very conclusively that, firstly, the removal of iron and aluminum is unnecessary, and, secondly, it is a dangerous step from the standpoint of accuracy in sulfur determinations.

Barium sulfate could be filtered after 24 hours

The next question studied concerned the method of adding $BaCl_2$ in precipitating the sulfates. Several procedures were tried; precipitating in cold, warm (about 50°F.), or in boiling solutions. The solutions were also boiled and kept on the steam bath for two hours; or, after precipitation in the cold the liquid was kept on the steam bath for 2 hours. In every case, the solutions were afterwards allowed to stand for at least 24 hours but were well stirred

TABLE 3

Effect of iron and aluminum chlorides on sulfur determination from ammonium sulfate solution

TREATMENT OF SOLUTION	AMOUNT OF $BaSO_4$ OBTAINED
	gm.
0.05 gm. ammonium sulfate alone	0.0914
0.05 gm. ammonium sulfate + 0.2 gm. $FeCl_3$	0.0908
0.05 gm. ammonium sulfate + 0.2 gm. $AlCl_3$	0.0909
0.05 gm. ammonium sulfate + 0.2 gm. $FeCl_3$ + 0.2 gm. $AlCl_3$	0.0909
0.2 gm. $FeCl_3$ + 0.2 gm. $AlCl_3$ (no ammonium sulfate)	0.0000

several times during the period. The results were practically the same in all cases. The only difference observed was in the physical condition of the precipitates. The samples that were precipitated in the boiling solution, or those heated on a steam bath for two hours, had much coarser particles than those obtained in cold or slightly warm solutions. At least, the settling of the precipitates was more complete and the supernatant liquid was clearer in the former than in the latter cases. Such mechanical differences are of some advantage in filtering either through asbestos or filter paper.

With small amounts present in ordinary soils, the precipitation of sulfur is a very slow process, especially when some silicates are present in solution. There is naturally the question as to how much time is required for a complete precipitation of sulfates, or, in other words, how long one should leave the precipitates stand before filtering. In order to answer this question, the solutions to which $BaCl_2$ was added were allowed to stand for one, two, four and eight days, respectively, before filtering. During the first 24 hours the solutions were stirred several times. The solutions that stood for longer periods were stirred once a day after the first day.

Results from four different soils are presented in table 4. They show that the precipitation is completed during the first 24 hours.

The filtering of barium sulfate may be done on a double thickness of "blue ribbon S and S" German filter paper, which holds the sulfate fairly well, or on some other suitable paper. The filtering through paper is, however, very slow. Besides, it requires considerable heat to burn the paper, and a high temperature tends to decompose barium sulfate. For this reason, Gooch crucibles with a good mat of long fiber asbestos and an application of moderate suction are recommended. It should be noted that asbestos sometimes persists in gradually washing out, i.e., the freshly made Gooch crucible may lose weight on repeated washing and drying. The prepared crucibles should come, of course, to a constant weight before they are used for the filtering of sulfates.

TABLE 4

Time required for complete precipitation of $BaSO_4$

SOIL NUMBER	NUMBER OF DAYS ALLOWED TO STAND BEFORE FILTERING THE PRECIPITATED $BaSO_4$			
	1 day	2 days	3 days	8 days
	gm.	*gm.*	*gm.*	*gm.*
3712	0.0070	0.0072	0.0073	0.0076
5133	0.0047	0.0037	0.0048	0.0048
5156	0.0020	0.0018	0.0025	0.0021
S3286	0.0122	0.0117	0.0118	0.0117

CONCLUSION

A method for sulfur determination in soils is presented which, for the past three years, has been successfully used at the Illlinois Experiment Station. It is a modification of the method described by Olson, as developed at the Washington Experiment Station. Some results are presented that justify the adoption of every step in the proposed procedure. Being a very short one, this method is well adapted for investigations where a large number of determinations are made.

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THE ALKALI SOILS IN HUNGARY AND THEIR RECLAMATION[1]

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After a short historical introduction on the reclamation work done in Hungary, dating as far back as the year 1769, the author discusses the different theories on the origin and specific character of alkali soils, and concludes, from his experiences, that for the genesis of alkali soils chiefly three factors are responsible.

These are namely: (*a*) the arid or semiarid climate, (*b*) an imprevious subsoil, (*c*) peculiar hydrological circumstances enabling an intermittent superabundance of moisture in the soil.

He points out, that alkali soils are not simply soils infiltrated by alkali salts. They represent rather a specific soil type of the arid climatic zone, and are the result of a peculiar chemical decomposition of the soil, derived from the effect of alkali salt solutions on the zeolitic and organic compounds of the soil. The displacing of the Ca ion by Na occurs because of the fact that the surface horizons are more or less poor in active calcium, and consequently the colloids of the surface layer percolate downward, forming a more or less impervious accumulation horizon under the alluvial surface horizon.

The washing out of alkali salts does not interfere with the alkali character of the soil. There are in Hungary many alkali soils, which are not harmful with their slight alkali salt-content, but are difficult to till, and unproductive on account of their bad physical properties. By direct experiments the author proved that in displacing the Na ions of the zeolitic-humic compounds by Ca ions, the impervious alkali soils could be changed into permeable soils of good tilth and texture. By infiltrating sodium salts and displacing the Ca ions of a productive neutral soil of good tilth and texture, the permeability and physical properties are made similar to those found in alkali soils, thus showing the artificial formation of an alkali soil.

The author treats of different types of Hungarian alkali soils, called "szik" soils, ranging them in different well defined groups and classes. He describes the territorial distribution of these different varieties, which make up a considerable part of the large plain, called "Alföld," which are mostly unproductive or very poor. He finds by geological, prehistorical, and historical statements,

[1] A short report on the author's Monograph, laureated by the Hungarian Academy of Sciences, Budapest and the Society of Hungarian Engineers.

that these territories were yearly more or less flooded by water, becoming dry again during the hot and dry summer period, thus causing the alkali salt to come to the surface by capillarity and changing the nature of the soil. But water logging was possible only where the filtration of water through the soil was prevented, either by some impervious clay subsoil, or by some calciferous hardpan, and where the water level in the subsoil was very near to the surface, even during the dry period.

In the early chapters the author deals systematically with the chief physical and chemical properties of the various "szik" soils. Numerous analytical and experimental data are given.

Summarizing these results he finds that the porosity of the heavy "szik" soils is very low, the water-holding capacity, on the other hand, is very high. The result is, that when saturated with water, the soil has no air capacity. This is one principal reason for its unproductiveness. The mechanical composition, though very different in the several types, is mostly very fine, the fine silt and clay making up the main part of the soil particles. Only a small part of it is of sandy character, but also in this case some kind of colloidal lime carbonate cements the coarse and fine sand. Thus the sandy soil becomes nearly impermeable to water, especially to a sodium carbonate solution, which is very abundant in this particular type of "szik" soil. As a whole the loamy and clay alkali soils are impermeable and their capillary power very deficient. Consequently the water movement in the soil is practically prevented. This is another reason for the unproductivity of these soils. As regards the plasticity and hardness of the soil, the heavy clay "szik" soils may be arranged in the highest class of Atterberg's classification. This explains the difficulty of tilling this type of soil. The high shrinking power of these soils causes the formation of very deep cracks or numerous fissures into which the muddy superficial floodings percolate, giving to the profile a peculiar veined appearance of irregular prismatic or columnar shape. The wilting coefficient is very high, accounting for the rapid extermination of any vegetation during the dry season.

As regards the chemical character of the different "szik" soils we have to arrange them in two main groups. In one group the aluminum silicates are superabundant, in the other, the lime carbonates. The latter are mainly black alkali soils, like the alkali soils in Fresno, Cal. The whole alkali territory lying between the Danube and Tisza belongs to this type of "szik" soil. On the other hand, the heavy clay "szik" soils along the Tisza river and its tributary streams are often lacking in carbonates and are mainly infiltrated by either sulfates like the alkali soil type of Billings, Montana, or sulfates partly intermixed with carbonate and chloride of soda, like the Salt Lake type of alkali in Utah.

The author also describes different methods of reclamation, dividing them into four groups according to their main characteristics, namely:

1. Physical reclamation methods
2. Methods of removing alkali
3. Chemical methods of reclamation
4. Biological methods of reclamation

The irrigation problem in Hungary before the war depended on the storing of water in the peripherical highland territories. As these water storing highlands have been cut off by territorial changes, physical and chemical methods are of most importance. These are methods of dry-farming, and consist of liming, manuring, tilling the soil, covering with a yellow marl, and draining surface-water to prevent the formation of earth crusts. In this way, a good wheat crop is harvested, but only a part of the "szik" soil is reclaimable in that way. By storing the rainfall in the spring, the alkali is washed deep enough in the subsoil so as to get a fair hay crop and good pasture, which is very important for cattle breeding in this dry country. With the limited irrigation water there is a successful system of surface irrigation requiring less irrigation water than the flooding system used in America. It is true, that the removal of alkali is slower and not so perfect as by washing through the soil. But the latter seems very often an insolvable problem, if we consider the impermeability of most of this alkali land. The establishment of fisheries on alkali land also was very successful and lucrative, considering the limitations of the fishing industry of the country. The reclamation work is now stopped chiefly because of lack of capital.

SOIL ACIDITY IN RELATION TO SOIL TYPE GROUPS, IN NACOGDOCHES COUNTY, TEXAS

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With the recent development of numerous field tests for the estimation of acidity, the relation of soil acidity to soil types is receiving a great deal of attention, particularly by those associated with soil classification work.

In order to obtain as exact information as possible regarding the prevailing soil reaction of the various types encountered in the field, the writer, in the course of the soil survey of Nacogdoches County, Texas (winter assignment 1923–1924) made over 200 acidity tests using neutral litmus paper[1] and the Soil-tex solution.

Nacogdoches County, in the central part of East Texas, lies entirely within the Interior Gulf Coastal Plain. The topography is rolling to hilly, the county as a whole being well dissected and well drained by numerous streams. The mean annual rainfall is 47 inches; the growing season about 240 days.

The soils of the county are derived from the unconsolidated sands, sandy clays, and clays of marine origin which constitute the underlying material of the Coastal Plain, extending from East Texas eastward across the Gulf states and well up along the Atlantic seaboard. The most extensive soils found in the county belong to the well-known Norfolk, Orangeburg, Ruston, Kirvin, and Susquehanna series. These are all upland types, having good regional drainage.

Concerning regional characters, these soils are low in organic matter, low in lime, and low in available plant-food. Under virgin conditions, these soils have 3 well-marked horizons, or soil layers, the lowest resting upon parent material. The first horizon consists of 2 or 3 inches of dark gray mineral soil, containing slight to moderate amounts of organic matter. The second horizon is well-oxidized and well-leached mineral soil, light colored, usually pale yellow to yellowish- or reddish-gray. The third horizon is the highly pigmented yellow, yellowish-red or red sand, sandy clay, or clay, characteristic of the region. The parent material immediately underlying these types is noncalcareous.

Inasmuch as the reactions of certain closely related types proved very similar, for the sake of brevity convenient groupings are made as follows:

1. Sandhills (Norfolk and Ruston fine sand).
2. Fine sands with sandy clay subsoils (Norfolk, Ruston and Orangeburg fine sandy loams).

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[1] H-ion concentration equivalents obtained from table prepared by E. A. Carlton, Mcdonald College, appearing in Soil Science, v. 16, p. 91, 1923.

3. Fine sands with clay subsoils (Kirvin fine sandy loam).
4. Fine sands with mottled, plastic clay subsoils (Susquehanna fine sandy loam).
5. Clay loam with mottled, plastic clay subsoils (Susquehanna clay loam).

Acidity tests were made of virgin soils only, and according to natural soil horizons. Particular care was taken to be certain the samples were representative. The mean acidity for each type group is shown graphically in figure 1.

It may be noted, at the outset, that the reactions of the first horizons are quite similar for the various soil groups represented. This condition appar-

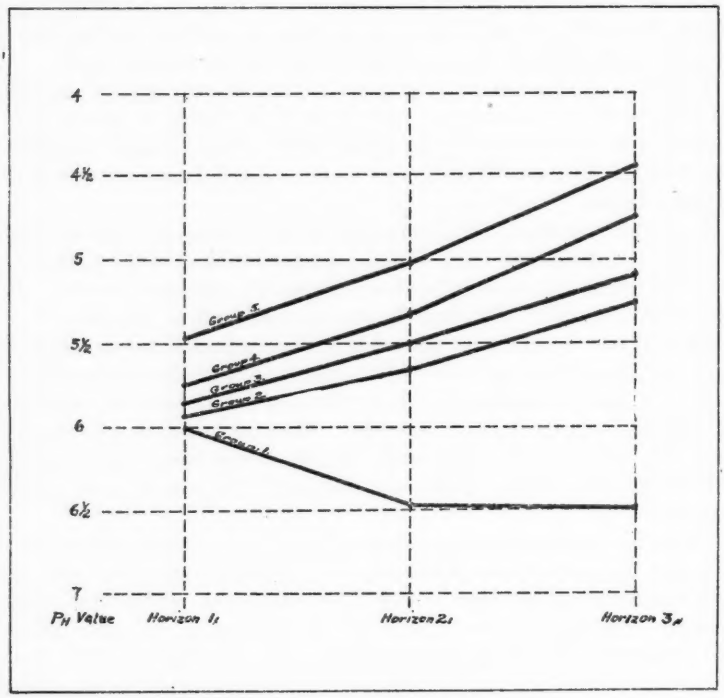

FIG. 1. MEAN ACIDITY FOR SOIL TYPE GROUPS

ently reflects the common character, namely, the surface organic layer. Below this horizon, the several groups vary, one from the other, in textural and structural character, and as regards aeration and internal drainage.[2] Correspondingly, the soil-reaction curves for the separate groups diverge, as shown, for increasing depths below the surface. Increasing acidity is invariably asso-

[2] For detailed descriptions of the soil types concerned, the reader is referred to Marbut, C. F., Bennett, H. H., Lapham, J. E., and Lapham, M. H., "Soils of the United States," U. S. Dept. Agr. Bur. Soils Bul. 96.

ciated with finer textures, poorer aeration, and poorer internal drainage conditions. Thus, the deep fine sands of the Sandhill group, which are deep, open-structured, well aerated and well drained, and without textural change in the 3-foot section, show the least acidity. The second group, consisting of 12 inches of fine sand overlying a subsoil of well oxidized, well drained, friable sandy clay, shows increasing acidity, most marked in the third horizon. Group 3, represented by a type consisting of 12 inches of fine sand, over a subsoil of well oxidized, well drained clay, shows a slightly higher acidity. Group 4, for which is used a type of fine sand 12 inches deep, overlying stiff, plastic clay, passing at 18 to 24 inches into a mottled plastic clay, with poor aeration and poor internal drainage, indicates a still higher acidity, becoming abruptly intense in the mottled subsoil. Group 5, represented by a clay loam, underlaid at shallow depths by a plastic clay, passing into a heavy, mottled, plastic clay deeper subsoil, with poor aeration and very poor internal drainage, shows the greatest acidity, the maximum of which is again found in the mottled subsoil.

Causes of variations in reaction within the soil type were found to be almost entirely traceable to discernible physical variations within the type. For example, areas occupying more gently sloping topographic position than usual were found to have a slightly higher acidity than normal for the type, probably due to increased organic content, finer textures, poorer internal and regional drainage conditions, or a combination of the above.

It further appears from this study, that the acidity relationship, as regards drainage conditions, depends more upon the internal drainage than upon the regional drainage. In support of this,—the highest acidity found in the county, (including many tests made of deoxidized lowland and swamp soils) was found existing in the Susquehanna clay loam, group 5, the tests being made at the tops of abrupt knolls in steeply rolling country.

Finally, it is apparent that, under climatic conditions tending to produce soils well leached of lime carbonates, it is entirely possible to estimate the mean acidity content of well developed, well weathered types, and to show fairly consistent differences between the acidity content of diverse types of this character.

THE CHEMICO-PHYSICAL INFLUENCES OF QUICK LIME AND CALCIUM CARBONATES ON MINERAL SOILS[1]

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The investigations of the last decade have brought us the fundamental knowledge of the effects of quick lime and calcium carbonate on the soil.

In carrying out the work reported in this paper, it was deemed necessary first of all to make a preliminary study of the chemical and physical phenomena of pure soil constituents. The native soils are of a complex composition, the constituents of which can hardly be isolated. Therefore its problems cannot be studied adequately unless the behavior of the separate soil constituents has been demonstrated by typical examples. Fine granulated quartz was used in the experiment as a representative of a widespread soil constituent, chemically almost inactive. Permutites were further used which, in comparison with the most active soil silicates, show only such differences as might be expected for gels of different ages and prepared by different methods. The greatest part of the experimental work was done by Hermann Sallinger, Josef Danzl and Hugo Junk. The summarized details will be published later.

I. ADSORPTION BY QUARTZ

Purified quartz with particles of a 0.002-mm. diameter was used in the following experiments. The effect of solutions on the quartz suspensions was studied by adding 50 cc. of solution to 50 cc. of suspension (containing 10 to 20 gm. of quartz), so that the total volume in each experiment was 100 cc. The quantity adsorbed changed considerably with the concentration. The figures mentioned for the adsorbed quantities concern solutions of 0.00224 normality. The values can be reproduced under identical experimental conditions. They are therefore transmittable.

1. Swelling values

The swelling value of a material is indicated by the concentration of a solution at which a quick settling of the suspended particles takes place. The knowledge of the swelling values is of importance in soil studies because it gives an idea of the effect of the material on the flocculation of the soil particles

[1] Translated from the German by N. Mogendorff and J. S. Joffe New Jersey Agricultural Experiment Station, New Brunswick, N. J.

and therefore of the formation and preservation of soil crumbling. This relation is to be considered in this way—the soil settles if the concentration of the solution of a compound is greater than the swelling value. However, well crumbled soils may be maintained at concentrations lower than the swelling value. The whole behavior of the soils indicates that there is a relation between the swelling values and the natural soil structure. Based on the swelling values of quartz the swelling values of the most important hydroxides of the bivalent metals [$Ca(OH)_2$, $Ba(OH)_2$, $Si(OH)_2$] are at a concentration of 0.00035*N*. For univalent metals (KOH, NaOH) the concentration is 0.1*N*. The effectiveness of the bivalent metals therefore is 300 times as great as for the univalent metals. Expressed in terms of weights, the amounts of the various substances necessary to flocculate a quartz suspension in 1 liter of solution are as follows:

	grams		*grams*
Calcium hydroxide	0.013	Potassium carbonate	3.5
Potassium hydroxide	5.6	Sodium carbonate	3.2
Sodium hydroxide	4.0	Magnesium carbonate	0.2
		Acid calcium carbonate	0.25

Thus the effectiveness of calcium hydroxide expressed in terms of weights is 430 times as great as that of potassium hydroxide, 300 times as great as that of sodium hydroxide, 266 times as great as that of potassium carbonate, and 245 times as great as that of sodium carbonate. The solubility of calcium carbonate is too little to measure the swelling value directly. The swelling value of acid calcium carbonate (0.009*N*) is about the same as that for calcium chloride (0.01*N*). In general the swelling values of the salts of many metals are about the same, for example:

Potassium carbonate	0.05*N*
Potassium chloride	0.045*N*
Sodium carbonate	0.06*N*
Sodium chloride	0.055*N*

The great differences which occur, if expressed in terms of weights, explain the different effects of the strongly active bivalent metals (Ca, Mg) against weakly acting univalent metals (K, Na). The detrimental effects of sodium carbonate on the soil are thus made clear.

2. Adsorptions

Quartz adsorbs strongly alkaline compounds. As far as soil problems are concerned these compounds are mainly hydroxides and carbonates. On the other hand, neutral salts and acids are taken up only in traces. To give an idea of the phenomena involved it will be satisfactory to note the quantities taken up by 1 kgm. of quartz (diameter 0.002 mm.) and also calculate it for an area of 1 hectare at the depth of 20 cm. (specific gravity 1.5). The quantities

adsorbed by quartz from 0.00224*N* solutions in grams and Doppelzentner[2] are as follows:

	1 KGM.	1 HECTARE
	gram	*dz.*
Calcium hydroxide	1.07	32
Potassium hydroxide	0.63	19
Sodium hydroxide	0.44	13
Magnesium carbonate	0.71	21
Potassium carbonate	0.42	13
Sodium carbonate	0.27	8
Ammonia nitrogen	0.07	2*

* Adsorption from ammonia; the ammonium hydroxide on account of its low ionic concentration is adsorbed only weakly from solution; ammonia (NH_3), if any, is taken up from solution only in minute quantities.

The variation in adsorption of hydroxides which could be repeated by various soil silicates, indirectly becomes of great moment in the case of liming with quick lime. Most of the contradictions with quick lime experiments, which could not be explained till now, may in all probability be traced to the phenomena mentioned.

II. EXCHANGE OF BASES

The processes of the exchange of bases in the soil have been studied in a constantly increasing measure for the last hundred years. In our experiments, rather homogeneous permutite was used, which was obtained from the Permutite Company (Permutit-Aktien Gesellschaft). It was produced by the wet process and is a sodium permutite with a low calcium content. The exchange of the bases of the permutite is subject to the following rules (in agreement with the processes in the soil):

The base exchange takes place in equivalent quantities. The taking up and giving off of the metals depends on the relation of the ions in the solution and differs for the various metals. Therefore, the metals combined in a permutite will exchange completely or incompletely for those present in the solution. The more easily a metal is taken up by a permutite and the more completely it is exchanged for combined metals there present, the more difficultly and incompletely will it be displaced from the permutite by other metals. If the metals investigated were arranged according to the quantities in which they were absorbed by the permutite they would form a successive series which, with a few transpositions, corresponds to the lyophilic series of colloid chemistry.

[2] A Doppelzentner = 100 kgm.

$$Mg < Li < Ca < Na < Ba < NH_4 < K < \ldots . H$$

Very probably hydrogen is the last link of this chain. The place of the metals in this series seems to be closely connected with the hydration of their ions.

Besides the exchange of bases between the ions of the solution and the silicate, other chemical or physical phenomena frequently enter which may influence strongly the course of the transformations.

The following rules may be established:

1. Neutral salts exchange in equivalent quantities (acid carbonates behave like neutral salts).

2. Hydroxides and alkaline compounds exchange in equivalent quantities, but at the same time there occurs the combination of hydroxides which can be traced back either to adsorption influences or to the formation of basic salts. In higher concentrations of hydroxyl ions, a chemical decomposition of the permutite silicates will result.

The action of soluble hydroxides and alkaline solutions on the silicates capable of exchange calls forth a change—which may be considered either as exchange of bases, adsorption, or decomposition of silicates, depending on the concentration of the solutions and the properties of the compounds present.

In the permutite experiments, hydroxides exchanged in equivalent ratio; at the same time approximately the same quantity of hydroxide was combined either by adsorption or by the formation of basic salts. It may be accepted as a rule, that from the hydroxide solution of a silicate, equal quantities of hydroxide are exchanged and combined. This, however, is true only for the silicates capable of exchange. Quartz and other soil constituents become active by their own adsorption.

The decomposing action of the hydroxides on permutites was detectable in the experiments only after longer periods (a few days). The course of these processes has not yet been studied.

III. ACIDS AND ACID-REACTING SOLUTIONS

Strongly active acids, namely solutions with a considerable hydrogen-ion concentration, bring about the decomposition of the silicates capable of exchange. It seems that partial decomposition of the silicates takes place in solution even at a low hydrogen-ion concentration. This is indicated by the formation of small quantities of aluminum and silicic acids in the solution; for the bulk of the silicate molecule an exchange of its cations with hydrogen is to be accepted, which means the formation of complex aluminum-silicic acids (permutite acids). This is corroborated by the fact that it is easy to restore permutites to their original effectiveness and constitution (regeneration of the permutite), by means of alkaline compounds if the loss of bases was the result of treating them with low acid concentrations. *The hydrogen of the permutite, on the other hand, is exchanged only very incompletely by cations of neutral salts.* This is a very important fact in soil fertility, since the formation of mineral acid soils is based on it. The occurrence of such formation is much more

frequent than is generally known and deserves more attention, especially in so far as it is related to the chemical transformations in the soil.

If permutites free from their basic cations (corresponding to the silicates of mineral acid soils) are treated with neutral salt solutions, an exchange of hydrogen for cations of the neutral salts will result first to a rather large extent; upon addition of more neutral salt solution, the exchange decreases quickly and soon it will be so small that it can be practically neglected. This solution shows an acid reaction corresponding to the titration-acidity of an equivalent amount of aluminum present in solution. The exchange will not stop with another addition of neutral salt solution, but it will be reduced to traces. This is also true in the case of potassium chloride solution (Daikuhara method). In general, all permutites possessing a cation hard to replace behave identically toward solutions with little of active cations (see series of cations). When a permutite free from its bases was treated 26 times with potassium chloride solution, only 2 per cent of the hydrogen was given off, which corresponds to the amount present in the permutite according to other analytical figures. This means that the methods formerly used for the determination of the acid content of a mineral acid soil furnish figures lower than the real content.

The exchange of the basic hydrogen for hydroxides and alkaline salts is, on the other hand, complete. The calculated hydrogen content and the quantity of ammonia taken up by the permutite was in agreement when the permutite was treated with ammonia, as mentioned above. It may be pointed out here that a treatment with ammonia solution is promising for the determination of acid in purely mineral soils. Approximately the right values may be obtained, as only very slight amounts are adsorbed from the ammonia solution. On the other hand, the strong adsorption which takes place from solutions of bivalent hydroxides—lime and barium hydroxide (Veitch method), will give figures double those indicating the true acid content of the soil.

Free carbon dioxide

The decomposition of the silicates depends on the concentration of free hydrogen-ions in the acids. Besides organic acids, carbon dioxide is active in the soil. The carbon dioxide[3] of the soil solution is practically completely dissociated into $H + HCO_3$ ions. The concentration of the carbon-dioxide ions is small and increases only slightly with increasing pressure of the carbon dioxide and its solubility in water which depends upon it. For soils and rocks the influence of the carbon dioxide may be considered as constant without introducing an appreciable error, even when the carbon-dioxide pressure is high (50 atmospheres and over).[4]

[3] Carbon dioxide (CO_2) very often called "carbonic acid" is a water-soluble gas, but only a small part of the dissolved CO_2 is combined with water under formation of carbonic acid (H_2CO_3).

[4] The solubility of carbonates under the formation of soluble acid salts (calcium, magnesium, or ferrous oxide) is influenced strongly with an increase in carbon-dioxide pressure.

The action of carbonic acid on permutite was investigated. It is very probable that the phenomena observed are also true for other silicates. The permutites are to be considered as the most unstable type of silicates. The attack by carbon dioxide is strong in the beginning but gradually decreases and goes on very slowly afterward. Water saturated with carbon dioxide at atmospheric pressure, lessened the normality of sodium permutite from 0.4526 to:

0.2104*N* if 1 liter was dripped on
0.1933*N* if 2 liters were dripped on
0.1940*N* if 3 liters were dripped on
0.0927*N* if 10 liters were dripped on

The decomposing action of the carbonated water was slight. It was indicated by the formation of small quantities of aluminum compounds and silicic acids in the solution. In the majority of permutites, sodium was exchanged for hydrogen, thus forming "permutitic acid."

Buffer actions

The investigations were concerned with mineral soils and dealt only with buffer actions in a classic sense, i.e., with the effects on the ion concentration in the solution and on the solubility of the compounds formed.

The acid carbonates of the soil solution exert strong buffer actions, inasmuch as the hydrogen-ion concentration of the free carbon dioxide is strongly forced back. The extent to which such an action may go is demonstrated by the fact that the "disbasing" of a permutite by water saturated with acid calcium carbonate (at 1 atm. CO_2 pressure) was forced back to 1/500 of the effects of salt-free carbonated water.

The buffer action of the acid carbonates in the soil is very evident. The upper layer of forest soils reacts (according to Gustav Krauss) almost always acid; this acid reaction diminishes quickly, however, in the deeper soil layers. On slight depth (5 to 10 cm.) the reaction is already neutral in most cases, while it will be faintly alkaline on greater depths. In regard to the relation of the rôle played by the carbonates in the soil, it is important to estimate besides the saturation of the free acid also the buffer action of the acid carbonates. This prevents largely the decomposition of the exchanging soil silicates and makes the exchange of bases safer.

Another process which influences the transformation of quick lime is the effect of alkalies present in the soil solution on the solubility of calcium hydroxide. Sodium hydroxide solution of 0.1 normality suffices to precipitate practically all the dissolved calcium hydroxide. Such high concentrations do not occur in soils, but much lower concentrations give evidence of this phenomenon, which accelerates the undesired effects of the alkali hydroxides.

Degree of saturation ("Sättigungsgrad") of soils

The influence on soil conditions exerted by the combining of metals has long since attracted attention. There is considerable difference between the effects of uni- and bi-valent metals. Calcium, magnesium, perhaps also aluminum and iron as bivalent metals; and the alkalies, chiefly sodium, as univalent metals; and further, hydrogen, are of importance for the soil. The first group accelerates the properties of settling and crumbling, and lowers the adhering qualities of the separate soil particles. The second group increases the coherence of particles, the soil gets more or less slimy, and the crumbling is less. A generally adopted definition for the "Sättigungsgrad" of a soil has not yet been established. Among the earlier investigators who studied the problem of soil saturation, Hissink (1) defines "Sättigung" or "Sättigungsgrad" of a soil as the difference between the adsorbable bases and those combined in the soil. Sokolovski (2) regards essentially only calcium, and means by "Sättigungsgrad" more or less saturation of the soil with calcium, thus considering his practical experience that the soil properties depend largely on the quantities of lime combined with the soil.

The unsaturated condition of mineral soils is evidently the result of freeing the soils from bases by acids, mainly carbonic acid. Therefore, it coincides predominantly with the rate of soil acidity. For soils rich in humus, the inadequately studied humic-acid compounds are to be taken into consideration. As yet no reliable method for the determination of the "Sättigungsgrad" of the soil has been found. On the basis of base exchange, pure mineral soils treated with ammonia, or in general with calcium-or barium-hydroxide solutions, give figures which serve as a guide for the determination of the saturation of the soil. On account of the high adsorption of bivalent hydroxides, the figures obtained should be halved. The working out of a reliable method for the determination of the saturation rate is a necessity for the study of the theoretical and still more the practical soil problems.

Adsorbability of exchangeable bases for plants

It is known that plants are able to absorb basic plant nutrients. A number of sand-culture experiments show that if the proper salts are present in the solution, the exchange of bases satisfies the nutritive needs of the plants. It is doubtful whether the plant roots are able to absorb directly basic nutrients from permutite bases without intervention of the exchanging salt solutions. Attempts to grow plants with permutites as the only source of available bases were not successful. Soil silicates incapable of base exchange but which could be decomposed by hydrochloric acid gave quantities of plant nutrients not even worth mentioning. It seems that the plant takes its nutrients only from compounds present in solution or from those which are made soluble by the exchange of bases (see Nostitz).

Quick lime and limestone fertilizing

The experimental results mentioned enable us to get an idea of the transformations which take place in the soil after an application of quick lime. These transformations are more complicated than they were believed to be until recently. They depend not only on the physical, but also largely on the chemical composition of the soil.

The flocculation effect of quick lime shows up when the swelling value in the solution has been reached. Compared with the swelling value of quartz, which is 0.013 gm. per liter, and assuming that the water content of the soil is 20 to 30 per cent by volume, this being the average water content for heavier soils, the quantity of calcium hydroxide necessary for the settling of 1 liter of soil (sp. gr. 1.5) amounts to from 0.0025 to 0.004 gm. This corresponds to an application of 5 to 10 kgm. of quick lime per hectare. This quantity, however, should be available in the soil solution in order to produce the desired physical action; it will correspond to approximately pH[5] = 10.5. It is known that when a soil has been flocculated once it can maintain the condition rather well, provided it is not disturbed by action of mechanical agents. Therefore, the soil crumbling will also be maintained when the hydroxide has been transformed by carbon dioxide to carbonate. It should be noted that the carbonate itself possesses properties which favor the formation of soil crumbles and it may be assumed that a certain quantity of dissolved calcium hydroxide has to be present in the soil in order to produce the desired physical action. For this reason an application of quick lime should be given at such a rate that a moderate excess remains in the soil solution. On account of the fact that an alkaline soil reaction is of disadvantage to the majority of crops, quick lime should be applied to the soil sufficiently early that the greatest part of the lime will have been precipitated from the soil solution as carbonate at the beginning of the growing process.

Adsorption and base exchange

Considerable quantities of calcium hydroxide are combined in the soil by adsorption and exchange of bases. The soil solution loses its bases by adsorption and becomes more or less inactive for the plants. The base is taken up from the soil solution and the alkaline reaction disappears or is considerably lessened without making the calcium inaccessible to the plant roots.

In relation to the exchange of bases it has to be considered whether a soil is more or less freed from bases, i.e., has an acid reaction. The result is an exchange between calcium and the basic hydrogen of the soil silicates and the formation of calcium silicates and water. This process improves the soil, the exchangeable silicates becoming more active in their chemical and physical properties through the replacement of the slowly acting hydrogen by the easily

[5] Translation doubtful. Interpreted "pH" without consultation with author.

transformable calcium. The exchange of bases is facilitated so that a mineral acid soil may be improved chemically, largely by an application of quick lime. On soils which are strongly reduced in bases, a quick-lime dressing is profitable.

If, however, the soil is rich in exchangeable potassium- and sodium-containing silicates, the results may be entirely different. Under these considerations calcium will replace potassium and sodium, which in their turn go into solution as potassium and sodium hydroxide. It is a well known fact that alkali hydroxides are harmful to plant growth if present in very small concentrations.

The alkali hydroxides are much less freely adsorbed by the soil, which is another reason why they are more active than an equivalent quantity of calcium hydroxide.

Compared with the quartz experiments the following computations may be deduced:

A weighed quantity of soil (1 kgm.) with the adsorbability of quartz was treated with solutions of 0.00224*N*, and it adsorbed:

Calcium hydroxide	1.07 gm. = 100 parts	
Potassium hydroxide	0.63 gm. = 59 parts	(1)
Sodium hydroxide	0.44 gm. = 41 parts	

The exchange of bases between the solution and the soil silicates proceeds, however, in gram-equivalents, namely $\frac{Ca(OH)_2}{2} = 37$; KOH = 56; NaOH = 40. For each 100 parts of calcium hydroxide adsorbed by the silicates, the following go into solution:

Potassium hydroxide	= 151 parts
Sodium hydroxide	= 108 parts (2)

The soil thus adsorbs:

Calcium hydroxide	= Difference (1) against (2)	—
Potassium hydroxide	= Difference (1) against (2)	−92
Sodium hydroxide	= Difference (1) against (2)	−67

In order to demonstrate this influence we might assume that when a soil with an adsorptive power equal to 100 parts of lime is treated with equivalent quantities of $Ca(OH)_2$, KOH and NaOH no lime will remain in the soil solution, but both potassium and sodium will be present in proportions of 60 and 67 per cent respectively. The alkalinity of the soil increases thus very much and is kept high for a long time, as the alkalies will not be precipitated by CO_2 as the lime is. Why the plants are injured when quick lime is applied to fertile soils, or rather to sand cultures is therefore easily accounted for. It is also clear why quick lime might cause severe injury to the crops if potassium fertilizers have preceded. The injurious factor in those cases is not the lime but the alkali hydroxides formed.

These facts lead to the rule, that quick lime should be applied at such a rate that the soil is able to adsorb the lime as well as the alkali hydroxides formed.

In order to use quick lime rationally one should be acquainted with the soil, its saturation rate and exchange of bases. It remains for the agricultural chemist to establish simple, practical and reliable methods for the determination of these magnitudes.

The decomposing influences of quick lime and alkali hydroxides on the silicates, as also the transformation of the adsorbed lime, have not yet been studied. That such processes do occur is indicated by the fact that the quantity of adsorbed lime increases considerably after hours and days. Nor has the behavior of mixtures of calcium and magnesium oxide and their hydrates (Graukalk) been studied. Not until these problems have been solved can one tell which is more efficient: large quantities of lime at long intervals, or small amounts with short periods between applications.

It is obvious that quick lime as a fertilizer has a very great influence on the soil; its effect is stronger than that of any other fertilizer. If the quick lime is applied to improve the soil structure, it should not be applied at a much higher rate than the soil can adsorb. Soils which are freed from bases are neutralized. Injury to the crops by the formation of alkali hydroxides may result after heavy quick lime dressing on soils of a good chemical composition. In both cases it is appropriate to apply a smaller amount than is indicated by computation figures. In any event the application should not be so much that the soil would not be able to adsorb the alkali hydroxides formed. Quick lime and potassium salts, especially kainit, should not be applied simultaneously, but with a proper period between. It is efficient to apply lime first and then the potassium fertilizer—for instance, lime in the fall and potassium salts the next spring.

IV. LIMING WITH CALCIUM CARBONATE (MARLING)

Calcium carbonate is a very insoluble salt, one liter of CO_1 free water nontaining 13 mgm. in saturated solution. On account of its low solubility its effectiveness has been ascribed exclusively to its easy transformability into the more soluble acid carbonate under the influence of the CO_2 to the surrounding air. The author thinks it a right presumption for the majority of the German soils, but the slight solubility of the carbonate itself can, under certain conditions, contribute to marked transformations, where acid-reacting soils freed from bases are involved.

Up to the present time the tendency has been to consider the difficultly soluble compounds quite apart from the more soluble substances, their chemical transformations having been regarded as "heterogeneous" reactions. It was assumed that compounds present in solution were acting on the insoluble solid phase. Only in more recent years did we succeed in showing that these processes of "homogeneous systems" proceed in relation to the solubilities of their reacting substances. The difficultly soluble substances go into solution again and again, so that considerable quantities may be transformed during a long period (3).

The occurrence of such transformations in soils have been suggested repeatedly. Their presence can also be shown for calcium carbonate.

If limestone is supplied to acid-reacting soils freed of bases, or to soils showing adsorbability, it will in part be dissolved in the soil solution, but it will be

precipitated out again whenever the solution comes in contact with soil particles which show an affinity for calcium carbonate. There is a continuous exchange of $CaCO_3$ between the soil solution and the soil particles. Solution and precipitation will continue until an equilibrium is reached. If solution and precipitation take place in separate places, their exchange in the solution will be established by salt-diffusion. In this way the exchange of $CaCO_3$ in the soil can go very far, notwithstanding its slight solubility, if only a relatively long time is available. The effectiveness of these processes cannot be expressed in figures, as they differ for every soil in nature and speed of reaction. It will be clear that the fineness of the limestone particles is of great importance. If equal amounts in weight of fine and coarse granulated limestone are applied to a soil, the space distance between the particles diminishes rapidly. The free distance between two particles is directly proportional to the diameter of the particles, assuming their percentage in the soil is the same. (This was calculated for watery suspensions of quartz, but in the same sense it is true for soil mixtures.)

It is generally stated that the smaller the particles of a substance the faster it dissolves. This statement is true only to a certain extent. The increase in solubility with decreasing size of the particle, as found theoretically, reaches for the size of soil particles values which hardly can be measured. On the other hand the speed at which the concentration of saturation is reached increases with the area of the soil particles, thus increasing strongly with decreasing size of the particles. The effectiveness of difficulty soluble fertilizers (lime and Thomas slag) depends, therefore, greatly on the size of their particles. It is clear that little effect may be expected, if the size of the particles corresponds to fine or medium-sized sand granules. Separate lime particles in the soil are effective only over a small distance (see appendix).

Through liming, lasting effects were obtained in the neutralization of acid soils, especially mineral acid soils, although its action was slow. The soil silicates which lost their bases by exchange, regained their activity, while the soil structure was improved at the same time. The neutralization of the soil acids is established by the transformation of calcium carbonate to acid calcium carbonate. The crumbling effect is not so great, as acid carbonates behave like neutral salts, while the concentration of most soil solutions does not reach the swelling value of the salt. On the other hand, extensive physical, perhaps chemical, influences are caused by the formation of $CaCO_3$ from $Ca(HCO_3)_2$. The equilibrium is established every time between the soil solution and the carbonates present in the soil. This equilibrium depends on the CO_2 content of the surrounding air. The CO_2 content of the soil air increases regularly with the depth. This increase causes a transformation of $CaCO_3$ to $Ca(HCO_3)_2$. which dissolves. A decreasing CO_2 content will cause the precipitation of $CaCO_3$. The latter will take place in dry periods and in arid regions when the soil water is raised and the soil solution, rich in acid calcium carbonate, rises to

the surface. Precipitation of $CaCO_3$ also takes place in soil layers where through greater diffusion large amounts of CO_2 are given off to the free atmosphere. This process appears everywhere as soon as the rising water movements take place in humid regions during dry periods. The result is the formation in arid regions of soil layers rich in lime. Very probably the calcium carbonate is precipitated in a colloidal form and crystalizes out later. The calcium carbonate is very finely divided during the intermediate state and can hardly be distinguished from a solution. In this form it can be absorbed to a great extent by all soil particles and thus it will possess a great crumbling effect. There are great differences in the use of quick lime and marl. The practical farmer considers their influence on the soil as identical, marl only being slower and milder in its action. This however will be the case only when the quick lime has been transformed into the carbonate by CO_2. As long as the quick lime is present as such, its physico-chemical influence is quite different from that of the calcium carbonate; it affects the soil equilibria to a very large extent.

Our studies are concerned only with the mineral soil constituents, but approximately the same results may be found with humic soil constituents, for instance, the influence of the acidity of humic substances upon soil organisms. The influence exerted by the quick lime on the inorganic and organic colloidal soil constituents will probably be of a similar kind, although it is not impossible that important differences may be found after a more careful knowledge has been obtained on this subject. It seems that certain humus substances which occur in old humus deposits, or in humus soils, have an unfavorable effect on plant growth when quick lime or even marl is applied. There are experiments on record where damage was done to the plants by an application of lime on old pastures or on soils bearing the first crop.

It should always be borne in mind that lime and marl are primarily soil improvers. As a plant nutrient they are of much less importance. The lime application should therefore be in agreement with the conditions of the soil. These conditions should be known as accurately as possible. When the necessary fundamentals of this knowledge have been established, the efficiency of the use of lime will be one of the most important factors for the improvement of the soil and of agriculture in general.

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APPENDIX

Size of particles in relation to fertilizing influences. The relations occurring in quartz suspensions served as a basis for the deduction of the spatial distribution of quantities of soil equal in weight but consisting of particles of different size.

The number of quartz particles (radius = $r\mu$) in m gm. of quartz (s.g. = 2.65) =

$$= \frac{10^{12} \cdot m}{\frac{4}{3} r^3 \pi \cdot 2.65}$$

Assuming that the particles are equally distributed in V cc. of water, the volume of the suspension will be

$$10^{12}\left[V + \frac{m}{2.65}\right]\mu^3$$

This is the volume of a cube whose edge is

$$L = 10^4 \sqrt[3]{V + \frac{m}{2.65}}\,\mu$$

L corresponds to $N = 10^4 \sqrt[3]{\frac{m}{4/3\, r^3 \pi \cdot 2.65}}$ particles.

For each quartz-sphere is thus available a length

$$l = \frac{L}{N}$$

$$l = \sqrt[3]{\frac{\left(V + \frac{m}{2.65}\right) \cdot 4 r^3 \pi \cdot 2.65}{3m}}\,\mu = 2.23075\, r \sqrt[3]{\frac{V}{m} + 0.37735}\,\mu$$

The smallest free distance between two quartz particles is therefore

$$a = l - 2r = 2r\left[1.115 \sqrt[3]{\frac{V}{m} + 0.377} - 1\right]\mu$$

Thus it is shown that the free distance between two particles is directly proportional to the diameter of the particles, assuming that the weight of quartz and the quantity of water in the quartz suspension remain constant.

This computation is also true for substances of different specific gravities and can also be applied, of course, to soil mixtures.

The area of soil particles, also compared with quartz, can be obtained as follows:

The weight of a quartz particle of spherical form with a radius = $r\mu$ is:

$$4/3\, r^3\, \pi \cdot 2.65 \cdot 10^{-12}$$

The number of quartz particles in 1 gm. of quartz is:

$$\frac{10^{12}}{4/3\, r^3\, \pi \cdot 2.65}$$

The area of 1 gm. of quartz is

$$\frac{4 r^2 \pi \cdot 10^{12}}{4/3\, r^3\, \pi \cdot 2.65}\mu^2 = \frac{3}{2.65\, r} \text{ square meters}$$

if r is expressed in μ.

If 2.65 is substituted by S as specific gravity in general, the formula obtains the general character:

$$A = \frac{3}{r\,S}$$

or, the area of the particles of quantities of a substance, equal in weight, is inversely proportional to the radius.

The effectiveness of difficulty soluble fertilizers, on one hand depends upon the area (speed of saturation and solution), and on the other hand upon the free distance between the particles (distance of diffusion).

THE ELECTRICAL CHARGE ON A CLAY COLLOID AS INFLUENCED BY HYDROGEN-ION CONCENTRATION AND BY DIFFERENT SALTS

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It is a well recognized fact that the physical condition of a soil depends to an important extent upon the colloidal state of the clay fraction, and it is of particular interest to learn how the reaction and the electrolyte content of the soil solution modify the state of dispersion of the clay. In such systems, one of the factors which is most effective is the electrical charge of the colloidal particles.[1] Recently Northrup and Cullen (8) have described an apparatus for measuring the cataphoretic charge of bacterial suspensions, and it occured to us that a similar procedure might be applied to a certain interesting colloidal clay, a supply of which was furnished to us by Prof. C. F. Shaw of the division of soil technology.

Since these experiments were completed, the writers have learned of the interesting investigations on cataphoresis and electric charge of soil colloids now being conducted by Bradfield (2), Mattson (7), Joffe and McLean (6), and Kelley[2] which will no doubt serve to develop this phase of soil colloid research. The present preliminary data are presented merely by way of suggestion, since they concern a very interesting, naturally occurring clay colloid and because the indirect as well as the direct effects of reaction on the cataphoresis of colloidal clay particles may be worth further discussion.

The clay employed in these experiments is described by Professor Shaw as follows:

> Last spring in connection with the soil survey work in the Lancaster area, I had occasion to go over the recently dried surface of the big desert playa known as Lake Rosamund. The surface of this lake is entirely flat and at every inundation it receives an increment of very fine sediments. You will notice that over 95 per cent consists of clay particles less than 0.005 mm. in diameter. As I saw the undried material in the lake, it consisted of a gelatinous material that had settled out from the original solution, leaving the supernatant solution practically clear. As the material became drier, it attained a more or less jelly-like consistency and gave every evidence of being colloidal in nature.

An approximate chemical analysis of a water extract of this clay was made by Prof. P. L. Hibbard, with the following results:

[1] It should be recognized, however, that the charge is not an inherent property of the colloidal particles, but may vary with the nature of the dispersing medium.

[2] Private communication.

Parts per million of dry material

	p.p.m.		p.p.m.
Ca	0	CO_3	420
Mg	0	HCO_3	1620
Fe	0	SO_4	2780
Na	5900	Cl	5600
		NO_3	positive test

In preparing the clay for the present studies, it was necessary to remove as far as possible all the soluble salts present. The clay was first sifted through a 200-mesh sieve, after which 40 gm. of the sifted material were shaken up thoroughly with 2 liters of distilled water. The suspension was then filtered in a Pasteur filter apparatus under pressure. Next the clay was scraped from the outside of the filter tube into a mortar, mixed with a little water, diluted again to 2 liters and shaken into a suspension. This suspension was titrated with 0.05 *N* HCl, with continuous shaking, until it came to equilibrium at approximately pH 5.0. The filtration through the Pasteur filter was repeated, residue again mixed with 2 liters of water and titrated with 0.02 *N* NaOH to pH 7.0 Finally the residue was washed six times with 2-liter portions of CO_2-free distilled water. The clay so prepared was made into a suspension according to the following procedure: About 10 gm. of the mud was mixed in a mortar with a little distilled water and this mixture was added to 3 liters of CO_2-free distilled water, the suspension shaken and filtered through a qualitative filter paper to remove any particles of sand or of organic matter. The filter paper was changed as soon as it started to clog. The suspension which passed through the filter paper was allowed to stand for 2 weeks, at the end of which time the heavier particles had settled out. These treatments yielded a translucent, amber colored suspension which was very stable. When viewed in a ray of sunlight, it had the dispersed appearance of a colloidal suspension. When coagulated by electrolytes a yellow, voluminous, jelly-like substance was precipitated. A portion of this suspension as finally prepared was tested qualitatively for the following ions: Ca, Mg, Cl, SO_4, Al, Fe and NO_3. A very faint trace of chlorine was found, but the other tests were negative. The specific resistance of the solution was approximately 935 ohms, and the pH value 8.5. It was found that the clay which settled out after long standing could be shaken up with more distilled water and a suspension formed which had the same conductivity, pH value and migration velocity as the original suspension. Obviously these treatments may have changed the chemical constitution of the original colloid, but for the purposes of this investigation, it was necessary to obtain a preparation freed as far as possible of di- and tri-valent ions and of contaminating salts.

A large number of preliminary experiments were made before it was found possible to develop a satisfactory technique for making the cataphoresis measurements. The apparatus employed was quite similar to that described by Northrup and Cullen, but several modifications were found advisable,

especially to provide stopcocks of as wide a bore as possible. It is quite probable, however, that a simplified form of a micro-cataphoresis apparatus would be more suitable for the purpose.

The clay suspension was supported in the cataphoresis apparatus on a 10 per cent sucrose solution, the latter being controlled so as to have practically the same electrolyte content and the same pH value as the suspension. The potential difference at the cell terminals was kept constant at 4 volts. The resistance of the saturated zinc sulfate in contact with the electrodes was considered negligible and since the distance between the 2 three-way stopcocks of the cell was 37 cm., the potential gradient was 0.108 volts per centimeter.

Each velocity measurement is computed as the sum of the distances over which the surfaces in two arms of the cell moved, one up and the other down, in a 10-minute interval. The measurements are expressed in terms of 0.5-mm. units, in which units the improvised cathetometer was calibrated. The accuracy of the measurements was dependent upon the exact control of conditions. Most important of all was the sharpness of the surfaces dividing the suspension and the sugar solution. Special comments are made later on the accuracy of individual measurements. The limiting error caused by mechanical difficulties and by bad surfaces was, in general, not greater than one-half of a velocity unit and was considerably less than this when sharp surfaces were obtained.

The pH values of the clay suspensions were always determined with the hydrogen electrode (Hildebrand type) and those of the sugar solutions were determined in some cases with the hydrogen electrode, and in other cases with the usual colorimetric methods. It was found impossible to determine the pH of the clay suspensions by the use of indicators, because of the remarkable combining or adsorbing capacity of this clay, which prevented the development of the normal color of the indicator.

EFFECT OF VARIATIONS IN pH ON THE VELOCITY OF MIGRATION OF THE COLLOID

In these experiments, in order to make negligible any effect of variations in total electrolyte content, NaCl was added to the suspension and to the sugar solution until both were of 0.01 *N* concentration with reference to this salt. Preliminary tests showed that at pH 8.5 (the pH of the suspension as prepared) and with NaCl present in 0.01 *N* concentration, the suspension travelled at a relative velocity of 6, and slight variations in the salt content did not produce any measurable change of velocity.

The clay suspension and the sugar solution to which NaCl had been added were each titrated to the desired pH values with a few drops of either 0.04 *N* NaOH or 0.04 *N* HCl as the case might be. After such addition of acid or of alkali, the conductivity of the solution was measured.

The velocity measurements at different pH values are given in table 1. It may be noted first that in every case the suspension travelled toward the

positive pole. There was no change in direction at any point between pH 2.1 and pH 12.7, which certainly covers the entire range found in soil solutions The velocity values from pH 5.0 to pH 10.0 are identical. At the extremes of acid or of alkaline reaction there was a decrease in velocity, but in these cases the cation concentration (H or Na) presumably became effective.

In the next experiments we made a series of velocity measurements for the purpose of determining the effects of various electrolytes in different concentrations. In every case the conductivity and pH values of the clay suspension and of the sugar solution were kept the same. The pH values of the suspensions were all 8.5, except when HCl, NaOH, $Ca(OH)_2$, Na_2CO_3, and $Al_2(SO_4)_3$ were used.

TABLE 1

Velocity of migration of clay colloid at different pH values

pH	RELATIVE VELOCITY	REMARKS
2.1	1	Readings at pH 2.1 to 4.1 were not sharp
2.4	2	
3.0	3	
4.1	5	
5.0	6	Readings at pH 5.0 to 10.0, inclusive, were sharp
5.4	6	
6.0	6	
7.0	6	
7.5	6	
8.5	6	
9.0	6	
10.0	6	
12.3	4	Readings at pH 12.3 and 12.7 were obtained with difficulty
12.7	0	

In all instances the suspensions migrated toward the positive pole. Every electrolyte used was effective in decreasing the charge of the suspension. The effective agent was primarily the positive ion, which is quite in accord with the fact that the suspension was negatively charged. The trivalent Al ion was most effective, followed by the H ion and the divalent Ca and Ba ions, and then by the monovalent Na and K ions. This order is, of course, the same as that usually obtained in colloid systems. With the higher hydrogen-ion concentrations, it remains to be determined whether the effect was produced by the hydrogen ions exclusively or whether other flocculating ions were brought into solution.

OTHER EXPERIMENTS

Clay suspensions which were washed with water until the electrolytes were reduced to a low concentration were found to have an increased velocity of

migration in the cataphoresis apparatus. This observation is confirmatory of the data already presented and is in agreement with other findings. Washing soils with distilled water nearly always tends to deflocculate them. Some years ago, Hoagland and Martin (5) observed that the withdrawals of solutes from the soil solution by growing barley plants caused significant changes in the amounts of material maintained in suspension when the soils were shaken up with distilled water. We may assume that the electrolytes present in the films surrounding the soil particles, as well as the nature of the latter, determine to a large degree the stability of the suspension.

A portion of the clay suspension was titrated very carefully with NaOH until complete coagulation was effected, care being taken not to add more NaOH than was necessary. The resultant mixture was then treated with an exactly equivalent amount of HCl and shaken into a suspension. The suspension so prepared was stable and did not coagulate on long standing. This

TABLE 2

Relative velocity of migration of clay colloid as influenced by different electrolytes

NaCl		Na_2SO_4		Na_2CO_3		NaOH		KCl		$CaCl_2$		$Ca(OH)_2$		$BaCl_2$		HCl		$Al_2(SO_4)_3$	
Concentration, milli-equiv.	Velocity	Concentration, milli-equiv.	Velocity	Concentration, milli-equiv.	Velocity	Concentration, milli-equiv.	Velocity	Concentration, milli-equiv.	Velocity	Concentration, milli-equiv.	Velocity	Concentration, milli-equiv.	Velocity	Concentration, milli-equiv.	Velocity	Concentration, milli-equiv.	Velocity	Concentration, milli-equiv.	Velocity
2.5	9	2.5	8	5.0	7	0.4	9	2.5	7.0	1.3	5	0.1	6	1.3	2	0.08	5	0.4	0
10.0	6	15.0	7	25.0	5	1.2	9	10.0	5.0	2.5	5	0.4	5			1.00	3		
20.0	5	30.0	5			20.0	4	20.0	4.5			1.2	5			4.00	2		
30.0	4	40.0	4			40.0	1	30.0	2.0							8.00	1		
40.0	2					60.0	0												
50.0	2																		

In all cases, the suspension migrated toward the positive pole.

experiment appears to show that for this clay suspension free from other electrolytes, NaOH had a greater coagulating effect than NaCl. It will also be noted from table 2 that NaOH had a greater effect in decreasing the velocity of migration than did NaCl. A similar experiment was carried out with $Ca(OH)_2$ and $CaCl_2$, and it was found that $Ca(OH)_2$ had a greater flocculating effect than $CaCl_2$.

The following experiment on the rate of settling was performed. To test-tubes, arranged in 6 rows, equal amounts of suspension were added. These different portions of the suspension were treated with successively increasing equivalent amounts of solutions of NaOH, NaCl, Na_2SO_4, Na_2CO_3, KCl, and $CaCl_2$, after which the tubes were thoroughly shaken and allowed to stand for 24 hours. The suspension had originally a pH value of 8.5 and all the solutions added, except those of NaOH and Na_2CO_3, were prepared so as to have the same pH values as the suspension. The divalent salt $CaCl_2$ showed by far the great-

est flocculating power. Among the monovalent electrolytes, the NaOH was considerably more effective than the others. KCl was next in order, but we did not find any significant differences in the flocculating powers of NaCl, Na_2SO_4, and Na_2CO_3. The general results of this experiment are entirely in accord with the determinations of the velocity of migration.

DISCUSSION

Several years ago, O. Arrhenius (1) made the interesting suggestion that clay may act as an ampholyte and display a behavior analagous to that of proteins, in accordance with the explanation of Loeb. The clay used in these experiments presented a different type of behavior. The cataphoresis measurements did not yield any evidence that this clay colloid possessed a definite iso-electric point (in the sense that a protein has an iso-electric point) within the range of hydrogen-ion concentrations which permitted the formation of a stable suspension. It is possible that the experiments of Arrhenius may be susceptible of other interpretations, as indicated by Bradfield.

It is a very common observation that soils in contact with a highly alkaline solution, such as occurs in most so-called black alkali soils, show extreme deflocculation, and become very impervious to water. It does not necessarily follow, however, that the clay colloids are stabilized directly by the excess of hydroxyl ions. When the reaction of a soil solution is changed, it is obvious that the conditions governing the solution of a number of chemical elements are likewise changed. When the reaction becomes sufficiently alkaline, there will be a marked tendency for the concentrations of several strongly flocculating ions to decrease, whether as a result of chemical precipitation or some other type of removal from solution. For this reason, an alkaline reaction would promote stabilization even if the hydroxyl ion itself had no effect. However, with some colloidal clay preparations, an increased hydroxyl-ion concentration tends to accentuate the coagulating effect of the various cations. An example of this is what Comber (4) calls the abnormal flocculation produced by $Ca(OH)_2$. Comber's explanation of this abnormal flocculating power rests on the basis of the precipitation of a protective colloidal silica compound which is precipitated only when the reaction of the medium is alkaline.

In a recent article, Mattson (7) presents an interesting discussion of the flocculation of clay colloids and of other colloids. He also reaches the conclusion that calcium may have an enhanced effect under conditions of alkalinity but his explanation is somewhat different from that of Comber. Mattson advances the suggestion that adsorbed ions act as "Verbindungsglieder" between the colloidal particles. Two negatively charged particles may, perhaps, be held together by a positive ion such as calcium, and, under some circumstances, an alkaline reaction may increase the number of "Verbindungsglieder," and thereby hasten coagulation.

It is quite apparent that several different considerations are involved in any explanation of the effect of reaction on the coagulation of clay colloids. Certainly, as just stated, we must first give attention to the changes in the concentration of the multivalent cations in the medium, as related to the hydrogen-ion concentration, before we can decide whether or not the hydroxyl-ion has a specific dispersive influence. For example, when the solution is made alkaline, there may take place a precipitaion of calcium, magnesium, iron, or aluminum, as hydroxides, carbonates, silicates, or phosphates, and the removal of these very strongly flocculating ions from solution may tend to increase the dispersion of the colloid or its electrolyte requirement for univalent bases. A further addition of alkali, such as NaOH, may cause flocculation because of the influence of the sodium ions when they attain a sufficient concentration. On the acid side, the question of the effect of ions formed as a result of the solution of certain components of the clay, must not be overlooked. These ions, as well as the hydrogen ion, may promote flocculation. When neutral electrolytes are added to the system, we meet with the additional complication of the well known exchange of bases. On this account, the solution in equilibrium with the clay may be different from that which is added. Bradfield has emphasized the great importance of hydrogen-ion concentration in its effect on the liberation of bases from a clay colloid. A further question also arises with regard to the inherent colloid properties of the new silicate complex formed when sodium replaces other ions, as distinct from the effect of the ions present in the solution. It is possible that a critical analysis of the direct and indirect effects of hydrogen-ion concentration on the dispersion of clay colloids may clear up some of the apparent contradictions in the literature. It may be expected that the effect of hydrogen-ion concentration on the liberation of bases will vary with different colloid preparations.

Mattson made a number of micro-cataphoresis measurements on clay colloids, without special control of the exact hydrogen-ion concentration, but he found that the colloid was negatively charged under all the conditions employed. It would also appear that his general conclusion in regard to the effect of hydroxyl-ion concentration on the dispersion of the colloid is similar to our own, in which connection the following quotation (7) may be cited:

> Die OH-ionen sind nicht an sich als die Bodenstructur beeinträchtigend zu betrachten. Die aufteilende Wirkung beruht vielmehr darauf, welche Kationen in der Bodenlösung überwiegen.

While it does not appear that clay possesses a definite iso-electric point in the same sense as a protein, it may still be possible for such a substance to show certain amphoteric properties when treated with strong acids or bases. The point which we wish to make now is that, within the range of reactions found in soil solutions, the clay colloid investigated by us showed no change in the sign of its electric charge, and the nature and concentration of the cations present in the solution had a predominant influence on the stability of the colloidal

suspension. Of course, in a soil other colloidal substances are present and these may not behave in the same way as the clay fraction. This would presumably be true of some of the organic colloids. Furthermore, Comber states that clay is readily flocculated by lime while fine silt is not.

A brief comment may be added concerning the bearing which the questions under discussion have on plant growth. It seems reasonable to assume that a highly alkaline reaction in the soil solution is unfavorable to the growth of most crops of agricultural interest. There are many reasons for this, including the direct effects of the increased alkalinity on root development, but the indirect effects are also of far-reaching importance. Not only may certain cations essential to plant growth be decreased in concentration to the detriment of the plant, but this same alteration on the soil solution may influence the physical state of the soil, and thus bring about a condition unfavorable to root development and to the activities of certain microörganisms.

SUMMARY

Measurements were made of the cataphoretic charge on a clay colloid as influenced by varying hydrogen-ion concentrations and by varying salts. It was found that the colloid remained negatively charged within the entire range of hydrogen-ion concentrations used (pH 2.1 to 12.7). The predominant factors determining the stability of the suspension were the nature and the concentration of the cations present in the medium. It is suggested that an alkaline reaction may sometimes cause deflocculation primarily because of the lessened solubility of di- and tri-valent cations, rather than because of the direct effect of the hydroxyl-ion concentration.

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THE DETERMINATION OF AMMONIA IN SOILS[1]

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A brief review of the literature on the determination of ammonia in soils indicates that there is no general agreement with reference to the best method. The object of this study was to investigate the errors involved in the determination, and the possibility of developing a more accurate method.

Potter and Snyder (6) investigated several methods and found that direct distillation of the soil with MgO causes liberation of some ammonia from organic nitrogenous compounds. They also found that complete recovery of ammonia which had been added to a soil could not be obtained by extraction with dilute HCl. They recommend the use of the Folin aeration method (2) with certain modifications, and indicate that good results were obtained when this method was used. The chief objection to this method is the time required.

Matthews (5) designed an aeration apparatus which shortens the time necessary for a determination but he found that in the case of some soils, complete recovery of ammonia added as $(NH_4)_2SO_4$ was not obtained.

Davisson (1) suggested a method by which the ammonia is obtained from soil extracts by very rapid aeration, using Na_2CO_3 and $Na_2C_2O_4$ to liberate the ammonia. The ammonia is first absorbed in a solution of H_2SO_4 and then the H_2SO_4 solution is distilled with MgO, in order to eliminate the error due to alkali being carried into the H_2SO_4 solution with the fine spray produced by the rapid current of air.

Gibbs, Neidig and Batchelor (4) modified the procedure recommended by Potter and Snyder by aerating the soil suspension for 1 to 1½ hours at a temperature of 75° to 85°C.

Valmari (8) recommended the use of a 0.5*N* NaCl solution for the extraction of ammonia from soils since he found that this treatment gives as much ammonia as is secured by dilute HCl extraction, and that the amount of organic nitrogen in most cases is much less in the salt extract than in the acid extract. Temple (7) has used a 1 per cent $CuSO_4$ solution to extract the ammonia from the soil. Both Valmari and Temple liberate the ammonia from the soil extracts by distillation with MgO.

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EXPERIMENTAL

The effect of hydroxyl-ion concentration on the liberation of ammonia from ammonium compounds and the formation and liberation of ammonia from organic nitrogenous material

It is reasonable to believe that the action of the basic compounds in the liberation of ammonia from ammonium salts and the formation and liberation of ammonia from organic nitrogenous material is roughly proportional to the concentration of the hydroxyl ions in solution.

The compounds which have been used by various investigators are given in table 1. The hydroxyl-ion concentration of each of them has been determined electrometrically and the data are expressed in terms of pH values.

Each of the compounds given in table 1 was added to 400-cc. portions of a solution containing 10 cc. of 0.02*N* ammonium sulfate. It was found that when $Ca(OH)_2$, K_2CO_3 and Na_2CO_3 were used all the ammonia was expelled

TABLE 1

Reaction of basic compounds

COMPOUND	STRENGTH OF WATER SOLUTION	pH VALUE
$BaCO_3$	Boiled suspension	9.00
$CaCO_3$	Boiled suspension	9.00
$MgCO_3$	Boiled suspension	10.00
Na_2CO_3	4 per cent	11.50
Na_2CO_3. NaCl	4 per cent Na_2CO_3—20 per cent NaCl	11.15
Na_2CO_3. NaCl	10.8 per cent Na_2CO_3—15 per cent NaCl	11.55
K_2CO_3	4 per cent	11.50
K_2CO_3. KCl	4 per cent K_2CO_3—20 per cent KCl	11.40
$Mg(OH)_2$	Boiled suspension	10.60
$Ca(OH)_2$	Saturated solution	12.60

in the first 100 cc. of distillate. It was necessary to collect 125 to 150 cc. when using MgO, 175 to 200 cc. when using $MgCO_3$, and 300 to 350 cc. when using $CaCO_3$ or $BaCO_3$. In all of these tests succeeding portions of the distillate were nesslerized to determine when the evolution of ammonia was complete.

When 1 gm. of any one of the compounds given in table 1 was added to 500-cc. portions of ammonia-free water containing 100 mgm. of any one of the following: acetamide, asparagine, alanine, cystine, glycocoll, guanidine carbonate, and "bacto peptone," it was found that amide nitrogen decomposed very slowly at 100°C. when the pH value of the solution was 10 or less, but that rapid decomposition occurred in solutions having a pH value higher than 10.5. At 42°C. under reduced pressure, amide nitrogen was stable in solutions of pH 11.5 or less, while in solutions above pH 12 slow decomposition occurred. Very little decomposition of amide nitrogen occurred when the various solutions were aerated at room temperature with basic compounds which gave pH values of 11.5 or less.

From these results it is evident that the ammonia can be secured from soil extracts either by distillation with $MgCO_3$ or by aeration with K_2CO_3 or Na_2CO_3 without any appreciable decomposition of organic nitrogenous matter. In testing several field soils it was found that practically the same result was secured when either MgO or $MgCO_3$ was added on distillation. This indicates the probable absence of amide nitrogen in normal soil extracts.

Extraction of ammonia from soil with salt solutions

Thus far it has been shown that ammonia can be completely liberated from a soil extract by distillation with MgO or $MgCO_3$ causing but slight decomposition of the organic matter. The chief difficulty, however, is to obtain by extraction all the ammonia which exists in the soil.

There are two ways in which ammonia may be held; namely, by adsorption and by chemical combination. It seems reasonable to believe that the addition of a salt of a strong base should increase the effectiveness of water in

TABLE 2

Ammonia extracted from a strongly acid soil

SOLUTION USED	AMMONIA EXTRACTED
5 per cent	*p.p.m.*
H_2O	5.25
$MgSO_4$	9.03
Na_2SO_4	13.20
$KC_2H_3O_2$	13.86
K_2SO_4	14.07
$CuSO_4$	15.96
KNO_3	16.80
$BaCl_2$	16.80

removing the ammonia from a soil by replacing the ammonia from insoluble ammonium silicates and also from that held by adsorption.

In order to find out how completely various salt solutions would replace the ammonia in soils, 50-gm. samples of a strongly acid soil and 250 cc. of various 5 per cent salt solutions were placed in pint jars and shaken in a mechanical shaker for 30 minutes. The suspensions were allowed to settle 10 minutes, were filtered on a Büchner funnel and 200-cc. portions of the filtrate were distilled with an excess of $MgCO_3$. The results given in table 2 are averages of closely agreeing duplicates. Shaking for 5 hours did not increase the amount of ammonia extracted.

More ammonia was secured from this soil by extraction with KNO_3 and $BaCl_2$ solutions than with any of the other salts used. Potassium nitrate does not form a precipitate on distillation and is much more desirable than $BaCl_2$ because all of the barium must be precipitated from solution before a sufficiently alkaline reaction can be secured to liberate the ammonia satisfac-

torily. This requires the addition of a large amount of MgO or $MgCO_3$. The heavy precipitate formed causes excessive foaming. A large amount of magnesium salts also is produced which lowers the hydroxyl-ion concentration of the solution and results in a slower liberation of ammonia on distillation. This objection applies to all divalent and trivalent compounds such as those of calcium, copper, iron and aluminum.

In the next experiment, a study was made in regard to the completeness of the extraction of ammonia from several soils by means of a 5 per cent KNO_3 solution. The ammonia content of the different soils was first determined by extraction with the salt solution. Then a known amount of NH_4OH was

TABLE 3

Recovery of ammonia from different soils by extraction with a 5 per cent KNO_3 solution

SOIL USED	SOIL REACTION	AMMONIA IN SOILS	AMMONIA ADDED	TOTAL AMMONIA IN SOILS	TOTAL AMMONIA RECOVERED	RECOVERY OF AMMONIA ADDED
		p.p.m.	*p.p.m.*	*p.p.m.*	*p.p.m.*	*per cent*
Kewaunee silt loam	Very acid	18.17	33.6	51.77	51.57	99.1
Carrington silt loam	Acid	9.66	33.6	43.26	43.26	100.0
Plainfield sand	Acid	4.41	33.6	38.01	38.01	100.0
Raw peat	Very acid	75.60	134.4	210.00	209.10	99.1
Decomposed peat	Neutral	45.30	134.4	179.70	179.70	100.0
Miami silt loam	Neutral	9.87	33.6	43.47	36.33	78.2
Black clay loam	Neutral	10.08	33.6	43.68	33.60	70.0

TABLE 4

Recovery of ammonia from soils by extraction with solutions of 8 per cent NaCl and 10 per cent KCl

SOIL AND REACTION	AMMONIA IN SOIL	AMMONIA ADDED	TOTAL AMMONIA IN SOIL	TOTAL AMMONIA RECOVERED		RECOVERY OF AMMONIA ADDED	
				NaCl solution	KCl solution	NaCl solution	KCl solution
	p.p.m.	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*per cent*	*per cent*
Miami silt loam neutral	13.23	16.8	30.3	29.23	29.23	95.2	95.2
Carrington silt loam, acid	10.96	16.8	27.76	23.94	26.92	77.2	95.0

added to another sample of each of the different soils and another extraction made. If this extract contained ammonia equal to the sum of the ammonia secured in the first extract and the ammonia added, the recovery of ammonia was considered 100 per cent. As in the previous experiment 50 gm. of dry soil, or 12.5 gm. of peat, was used. The results are given in table 3.

A rather low recovery of the ammonia was obtained from the Miami silt loam and the black clay loam by extraction with a 5 per cent KNO_3 solution. When the black clay loam was ground to pass a 200-mesh sieve and extracted with a 5 per cent KNO_3 solution, 80 per cent of the added ammonia was recovered. When a 10 per cent KNO_3 solution was used, a recovery of 93.5

per cent of the ammonia added was secured. Since it is necessary to use a large amount of salt to completely extract the ammonia from some soils, a comparison of NaCl and KCl was made, using approximately equal molecular amounts of each salt. Fifty-gram samples of soil were shaken 30 minutes with 500 cc. of an 8 per cent solution in case of NaCl and a 10 per cent solution in case of KCl. It was found that NaCl and KCl were equally effective in the extraction of ammonia from a neutral soil, but in the case of the acid soil the KCl was more effective. The results are given in table 4.

In another experiment using two soils which had been incubated 7 days with 2 per cent of dried blood, it was found that a 10 per cent KCl solution (1 part soil to 10 parts of solution) extracted about 5 per cent more ammonia than a 10 per cent NaCl solution or a 5 per cent HCl solution. A 1 per cent $CuSO_4$ extract yielded about 5 per cent less ammonia than the 10 per cent NaCl extract. When these soil suspensions were aerated with K_2CO_3 the ammonia secured was from 1 per cent to 5 per cent more than that secured from the 10 per cent KCl extract. A 20 per cent KCl extract gave practically the same results as those secured by aeration.

Recovery of ammonia added to soil as ammonium hydroxide and ammonium sulfate

Potter and Snyder (6), Matthews (5), and Gibbs, Neidig and Batchelor (4) in order to test the efficiency of the aeration method, added ammonia as $(NH_4)_2SO_4$ to the soil before aerating. It was found in this investigation, using the aeration method, that ammonia added to a Miami silt loam soil as $(NH_4)_2SO_4$ could be recovered more completely than ammonia added as NH_4OH. The data are given in table 5. The rate of aeration was about 200 liters of air per hour. Tubes 1½ by 14 inches were used to hold the soil suspensions. Much better agitation was secured in the tubes than in Kjeldahl flasks.

When the ammonia added to this soil was determined by extraction with a 10 per cent KCl solution and distillation of the extract with MgO, 99 per cent of the ammonia added as $(NH_4)_2SO_4$ and 90 per cent of the ammonia added as NH_4OH were recovered. It is evident from these data and those given in table 5 that ammonia is more strongly absorbed by a soil when it is in the form of NH_4OH than when it occurs as $(NH_4)_2SO_4$. Therefore, in order to test the efficiency of a method for determining ammonia in soils, the ammonia should be added to the soil as NH_4OH, since ammonia and not ammonium sulfate is formed in the process of ammonification.

Comparison of extraction with potassium chloride and aeration methods

In these experiments comparisons were made using three different procedures, as follows: extraction of the soil with a 20 per cent KCl solution and distilling the extract with MgO; aeration of the cold soil suspension for 8 hours

with a solution containing 4 per cent K_2CO_3 and 20 per cent KCl; and aeration of the soil suspension at 75°C. with 2 per cent Na_2CO_3 solution (6).

The results of the first experiment are given in table 6. Complete recovery of ammonia added to these soils could not be secured with a 5 per cent KNO_3 solution.

The data given in table 6 agree with those given by Matthews (5) and show incomplete recovery of ammonia from some soils by the aeration method. When the same soils were extracted with a strong salt solution a satisfactory recovery of the ammonia added was secured in all but one case.

In the second experiment the ammonia content of a Miami silt loam soil was determined by the three different procedures. A 10 per cent solution of KCl was used instead of a 20 per cent solution as in the previous experiment.

TABLE 5

A comparison of the recovery of ammonia added to a soil as NH_4OH and $(NH_4)_2SO_4$, by aerating with a 4 per cent K_2CO_3—20 per cent KCl mixture

SOIL USED	AMMONIA ADDED	RECOVERY OF AMMONIA AT END OF			
		4 hours	8 hours	12 hours	22 hours
	p.p.m.	*per cent*	*per cent*	*per cent*	*per cent*
Miami silt loam	67.2 as NH_4OH	76	80	84.0	84.5
Miami silt loam	67.2 as $(NH_4)_2SO_4$	89.5	91		93.8

TABLE 6

Recovery of ammonia added to soils by aeration with a solution of 4 per cent K_2CO_3 and 20 per cent KCl and by extraction with a 20 per cent KCl solution

SOIL	AMMONIA ADDED	RECOVERY OF AMMONIA BY AERATION	RECOVERY OF AMMONIA BY EXTRACTION
	p.p.m.	*per cent*	*per cent*
Garden soil	33.6	89.0	99.0
Alkaline peat	33.6	80.0	88.0
Alkali soil (California)	33.6	72.0	95.8
Alkali soil (California)	33.6	81.0	97.9

In order to determine if each of the different methods had completely removed the ammonia from the soil and also if the treatments involved cause an appreciable formation of ammonia from the decomposition of organic matter, the determinations according to the different methods were repeated several times successively on the same sample of soil. Ammonia-free water was added to the hot soil suspensions to replace that lost during each determination. The amounts of ammonia secured by extraction with KCl and by aeration of the cold soil suspension were nearly the same. Further extraction and aeration gave only very small additional amounts of ammonia. Similar results have been secured on a large number of soils.

When the Miami silt loam suspension was aerated at a temperature between 70 and 75°C., the amount of ammonia secured was almost twice as great as that secured by the other methods. The total ammonia obtained by the second

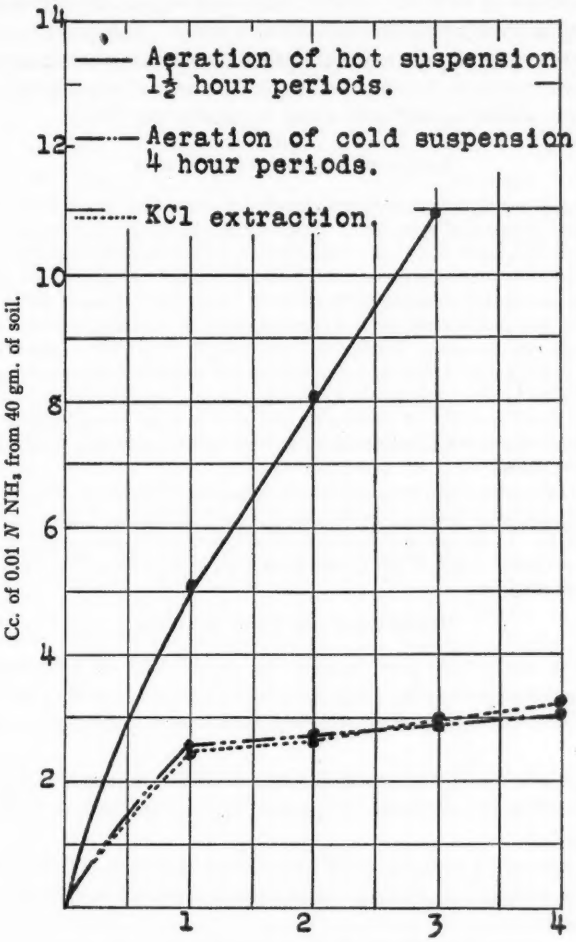

Fig. 1. Comparison of ammonia secured from a soil by successive determinations with different methods.

and third successive determinations by aeration at 75°C. was greater than that secured by the first determination, which indicates that there was considerable formation of ammonia from the organic nitrogen in the soil. The results are plotted in figure 1.

The sharp break in the curves plotted from the data obtained by extraction and by aeration of the cold suspension, indicates that practically all of the ammonia was secured in the first determination. When the soil was aerated at a temperature of 75°C, it is evident that some organic nitrogenous matter was decomposed and ammonia produced as a result. This procedure is probably entirely satisfactory for ammonification experiments where large amounts of ammonia are secured, but it cannot be used for an accurate determination of the ammonia content of field soils which is usually very low.

Analytical procedure recommended

Pulverize and mix the soil thoroughly by passing it through an 8-mesh sieve. In case of dry soils, grind to pass a 60-mesh sieve. Weigh out 50 gm. of soil (12.5 gm. in case of dry peat) and place in a quart Mason jar. Add 500 cc. of a 10 per cent KCl solution (in case of neutral or alkaline soils use a 20 per cent KCl solution); shake for 30 minutes in a mechanical shaker; allow to settle 10 minutes and filter on a large folded filter. Transfer 400 cc. of filtrate to a Kjeldahl flask, add a small piece of paraffine to prevent foaming and a little 20-mesh limestone to prevent bumping. Distill with 1 gm. of MgO. Catch 125 cc. of distillate in 10 cc. of 0.02*N* H_2SO_4, boil to expel CO_2, cool and titrate with 0.02*N* NaOH using methyl red as an indicator. If the amount of ammonia is less than 2 mgm., nesslerization is recommended. Add 50 cc. of distillate to 2 cc. of Nessler's reagent, allow to stand about 5 minutes and compare in a nessler tube with standards made up at the same time containing from 0.1 to 0.6 cc. of 0.01 *N* $(NH_4)_2SO_4$.

In case of soil extracts from ammonification experiments, distill 250 cc. of the extract with 1 gm. of MgO and catch 125 cc. of distillate in 25 cc. of 0.2*N* H_2SO_4. Titrate the excess acid with 0.2 *N* alkali. In the case of soil extracts which contain large amounts of easily decomposable organic matter, 1 gm. of $MgCO_3$ may be used in place of MgO, 175 cc. of the distillate being then collected.

Discussion of analytical procedure

The above method has given satisfactory results both on field soils and in ammonification experiments. Soils treated with 10 per cent KCl solution can be shaken and allowed to stand over night without any change in ammonia content.

A filtered solution of commercial muriate of potash is recommended for use in the extraction of ammonia. Impurities such as magnesium salts are not objectionable.

Filter paper often contains small amounts of ammonia. These should be removed by boiling the paper in distilled water if small amounts of ammonia are to be measured.

Ammonia-free water can be readily prepared by redistilling ordinary distilled water to which has been added a little $KHSO_4$.

Nessler's reagent is prepared according to Folin (3) as follows: Dissolve 150 gm. of KI in 200 cc. of distilled water, add 200 gm. of HgI_2 and when this is in solution make up to 1 liter, filter and dilute to 2 liters. Add 750 cc. of this solution and 750 cc. of distilled water to 3500 cc. of 10 per cent NaOH prepared by dissolving 375 gm. of NaOH in 600 cc. of distilled water. Allow the carbonates to settle, decant the supernatant liquid and dilute to 3500 cc.

In case of neutral or alkaline soils a 20 per cent KCl solution is recommended to insure more complete extraction of the ammonia from the soil.

SUMMARY

A study of the various methods for determining ammonia in soils has been made. The pH values of the various compounds which have been used for the liberation of ammonia were determined. It was found that amide nitrogen decomposes slowly at 100°C. when the pH is 10 or less. If the pH is 10.5 or higher, rapid decomposition takes place at 100°C. At 42°C. under reduced pressure amide nitrogen is stable at pH 12 or less. These results show that ammonia can be secured either by distillation with magnesium carbonate or aeration with potassium carbonate without appreciable formation of ammonia from the decomposition of organic matter.

Various salt solutions were used to extract the ammonia from soils. It was found that a potassium chloride solution is the best for this purpose. Extraction with a 20 per cent potassium chloride solution gives practically the same amount of ammonia as aeration of a cold soil suspension containing 4 per cent potassium carbonate and 20 per cent potassium chloride. Aeration of a soil suspension at 75°C. containing 2 per cent sodium carbonate caused the formation of a considerable amount of ammonia from the organic nitrogen in the soil.

It was found that ammonia added to a soil as ammonium hydroxide was more difficult to recover than ammonia added in the form of ammonium sulfate.

A simple and rapid method was developed for the determination of ammonia in soils. A strong potassium chloride solution is used to extract the ammonia from the soil. The extract is then distilled with magnesium oxide to liberate the ammonia.

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